REACTOR
FUEL
PROCESSING

A Quarterly Technical Progress Review

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

July 1960

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REACTOR FUEL PROCESSING

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foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Office of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, A. A. Jonke, S. Lawroski, W. J. Mecham, W. A. Rodger, W. B. Seefeldt, V. G. Trice, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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REACTOR FUEL PROCESSING

Specifications for Returned Uranium Hexafluoride

On Apr. 2, 1960, the AEC published in the *Federal Register*[1,2] a notice setting forth information on its charges, specifications, packaging and handling data, and other information on enriched and depleted uranium hexafluoride. These data do not differ from those previously in effect. However, some of the information has not previously been published in the *Federal Register*. The specifications for uranium hexafluoride to be returned to the AEC are as follows:

1. Enriched uranium furnished as UF_6 shall consist of at least 99.0 wt.% UF_6. The impurities making up the remainder may consist of fluorocarbons, hydrogen fluoride, and certain cations. The material shall be free from contamination by hydrocarbons, partially substituted halohydrocarbons, or chlorocarbons.

2. Total pressure of a filled cylinder held at $200°F$ until all material is liquefied shall be less than 75 psia.

3. The following cation impurities shall not be exceeded, as determined by spectrographic analysis:

Cation impurity	Parts per million parts of uranium
Boron	8
Beryllium	0.3
Lithium	10
Antimony	1
Ruthenium	1
Niobium	1
Tantalum	1
Titanium	1
Total cation impurities	300

4. Bromine content shall not exceed 1 part per million parts of uranium, and chlorine content shall not exceed 100 parts per million parts of uranium.

5. Mole fraction of impurities, as determined by freezing-point depression, shall not exceed 0.01 mole fraction.

6. Total nonvolatile matter shall not exceed 500 parts per million parts of uranium.

7. Boron equivalent neutron cross section of total impurity elements, as determined by thermal-neutron absorption, shall not exceed 8 parts per million parts of uranium.

8. The maximum individual concentrations of molybdenum, chromium, vanadium, and tungsten shall not exceed 200 parts per million parts of U^{235}.

9. The total gamma activity due to fission products and U^{237} shall not exceed 20 per cent of the activity of aged natural uranium.

10. The beta activity due to fission products shall not exceed 10 per cent of the activity of aged natural uranium.

11. Plutonium content shall not exceed 1 part per billion parts of uranium.

Domestic Uranium Production

The AEC announced statistics[3] on domestic uranium production for the last six months of the calendar year 1959. Domestic ore reserves were estimated to total 86,100,000 tons on Dec. 31, 1959. In addition, ore stockpiles totaled 1,449,069 dry tons. Ore receipts at all private plants and government purchase depots in July–December, 1959, totaled 3,614,000 dry short tons; and ore fed to process totaled 3,623,000 tons, with an average grade of 0.24 per cent U_3O_8. Uranium concentrates received at the Grand Junction depot totaled 7899 tons of U_3O_8 in the six-month period.

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As of Jan. 1, 1960, there were 25 uranium processing mills operating in the western United States, including the Cotter Corporation mill at Canon City, Colo., which was being enlarged from a pilot plant to a 200-ton-a-day mill. One Wyoming mill (Globe Mining Company) had started up, but the first concentrate was not delivered to the AEC until early February 1960. The only government-owned mill, at Monticello, Utah, was closed at the end of the calendar year 1959. The combined rated daily capacity of the 25 mills was 22,100 tons of ore per day, and their total estimated capital investment was about $142 million.

AEC Processing Survey

The AEC has announced that it has temporarily halted plans to expand existing chemical processing facilities at its Hanford, Oak Ridge, Savannah River, and Idaho Falls sites, pending the results of a survey it is making of industrial plans to enter the field.[4] Of particular interest is the privately sponsored feasibility study being conducted by the Industrial Reprocessing Group, made up of the Davison Chemical Division of W. R. Grace and Co. and five utilities with atomic plants planned or under construction.[5] The AEC has also asked utilities with reactor projects to assess the impact a delay in the availability of processing facilities would have on their power costs in terms of the added lease charges and cost of storing irradiated fuel. An AEC decision on its future construction plans is expected this summer.

Regulations Concerning Criticality During Shipment

On Oct. 30, 1959, the Bureau of Explosives, which formulates Interstate Commerce regulations for the shipment of radioactive and fissionable materials, set forth a rule on the shipment of fissionable materials. This rule states in part, "The use of so-called bird cages constructed with an open framework shall be restricted to exclusive carload or truckload shipments. Bird cages should be designed so as to prevent telescoping of other containers within the framework." In January of this year the Bureau of Explosives gave oral approval to a comparatively inexpensive way of conforming to

this rule. Shippers of such materials have had the option of containing the bird cages in wooden or metal boxes which appreciably adds to the weight and hence the cost of the shipment, or of using the exclusive carload provision of the regulation which also usually involves an added expense. Under the new interpretation of the rule, the Bureau of Explosives will now permit the bird cage to be enclosed in heavy-gauge hardware wire which is sufficiently strong to prevent two or more bird cages interlocking upon impact, provided the arrangement has been approved by the Bureau. This avoids the premium charges of enclosing the bird cages in a wooden or metal box or in exclusive carload shipments.[6]

On Mar. 17, 1960, the AEC published in the *Federal Register* additional regulations designed to protect against criticality and radiation exposure during shipment of irradiated fuel elements.[7] The proposed regulation is part of Title 10, Code of Federal Regulations, Part 72.

Shipping casks which are expected to cost as much as $100,000 each must be constructed to maintain their structural integrity under all conditions of shipment and under conditions of severe impact. The licensee must demonstrate that the mass of fuel shipped will be limited in such a manner that criticality will not occur. One measure required by the regulations to prevent meltdown is to allow the fuel elements to be shipped only after they have cooled long enough to assure that, when the casks are loaded, the maximum temperature of the fuel elements will remain well below their melting points.

Under the proposed regulation each licensee making application to transport any number of irradiated fuel elements outside of his authorized location of use or to deliver such material to a carrier must submit to the Commission engineering drawings, experimental data, and technical references showing that the cask to be used is designed for safety from the standpoint of criticality, heat transfer, shielding, and structural integrity.

Regulations published in the *Federal Register* are inoperative for a period of 30 days during which interested parties may file written comments or objections. It is understood that, during the first week in April, the American Standards Association formally requested the AEC to extend the period of comment, relative to the regulation in question, an additional 60 days.

Waste-Disposal Licensing

The AEC has determined that regional disposal sites for permanent disposal of low-level packaged radioactive waste materials shall be established, as needed, on state or federal government-owned land.[8] Preliminary to the selection of regional sites, the Commission would conduct detailed studies of the geologic, hydrologic, and topographic factors in connection with any proposed site in order to ascertain that a proposed site would retain the buried materials without contamination of the environment. Once a site is put into use, monitoring procedures will be established to ensure that the operations are performed in a manner which will not endanger the surrounding area.

The Commission does not contemplate that the ownership and control of the sites must necessarily be restricted to the federal government. As the atomic energy industry grows and the need for new sites is established, the Commission anticipates that state governments may wish to assume some responsibility in the establishment and control of sites for the benefit of their citizens.

The publicly owned disposal installations would be operated by private contractors or licensees under strict government controls or by the federal or state government and would be available to all users of radioactive materials. Land requirements for disposal sites will not be large, as evidenced by the fact that over the last 15 years low-level solid or packaged wastes at Oak Ridge have been handled in approximately 60 acres. On the basis of this experience, it is estimated that all such wastes generated between now and 1980 in the 16 states in the Northeast could be disposed of in a 200- to 300-acre site.

It is expected that the first regional site will be needed in the northeastern part of the country where there is a relatively heavy and growing concentration of industrial, medical, university, and other users of radioisotopes. The needs of other regions will be met later on as they develop.

The Coastwise Marine Disposal Company of Long Beach, Calif., continues to have its troubles. In January of this year the City Council of Long Beach denied a business license to this firm and issued a cease and desist order, charging that the proximity of their waste storage yard to a school constituted a safety hazard.

The owner of the company, Robert Boswell, was booked in the Long Beach Municipal Court on the charge of operating a junk business without a license.[6]

In March the Los Angeles Superior Court upheld the right of Coastwise Marine Disposal Company to engage in this business of collecting, packaging, and disposing at sea of low-level radioactive waste, pursuant to a proper AEC license. The Court thus invalidated action taken by the Long Beach City Council to deny Coastwise Marine a city business license.

The Court's decision read in part, "The Atomic Energy Commission has been granted full power and full responsibility for regulating the disposition of radioactive waste and protection of public health thereby. Congress has decreed that the Commission may not delegate regulation of such waste disposal even to a state. Therefore, the city of Long Beach is without power unreasonably to interfere with those activities of the plaintiff for which he is licensed by the Atomic Energy Commission."[4]

In April, however, the AEC directed the holding of a public hearing in Los Angeles on May 9, 1960, at which time Coastwise Marine was to show cause why the company's license to receive, package, and dispose of radioactive waste should not be revoked. Ten specific violations of AEC rules are documented in the AEC order.[9]

The Walker Trucking Company hearings[10] scheduled for Feb. 9, 1960, were first postponed and then rescheduled for June 14, 1960. Hearings on alleged violations of radiation-safety regulations[11] by Mines Development Company, Edgemont, S. Dak., were rescheduled for May 17, 1960.

Survey of Sea Disposal Sites

The AEC has signed a contract with Cleveland Pneumatic Industries, Inc., of Cleveland, Ohio, for a year-long study of underwater conditions at two established waste-disposal sites off the California coast.[12] This is a follow-up of an earlier survey of the two areas, in April 1957, which did not disclose any detectable amounts of radioactivity attributable to waste-disposal operations even in the immediate vicinity of the older of the two sites.

The new survey will be carried out by the contractor's Advanced Systems Development Division, of El Segundo, Calif., and again will

seek to measure the radioactivity, if any, resulting from the disposal of low-level packaged radioactive wastes at the two locations. The company will have associated with it, in an advisory capacity, members of the staff of the Scripps Institution of Oceanography at La Jolla, Calif.

The older of the two waste-disposal areas is centered at approximately 37°39′ north latitude and 123°26′ west longitude, a point in the Pacific Ocean about 52 statute miles west of San Francisco. Disposal activities have been carried out there since 1946. Approximately 21,000 concrete-encased steel drums and 300 concrete boxes containing some 14,000 curies of radioactivity at the time of disposal have been deposited at the site.

The second site is in the Santa Cruz Basin, the center of which is approximately 33°39′ north latitude and 119°28′ west longitude, a point some 53 statute miles south of Santa Barbara. Since 1953, 2950 drums containing a total of 60 curies of radioactivity has been placed at this location.

All disposals of radioactive waste at these sites have been made in depths of 1000 fathoms or greater, or more than a mile deep.

Two oceanographic field surveys will be made at each disposal area at six-month intervals. The first cruise was scheduled to begin Mar. 8, 1960. Estimated total cost of the study is nearly $60,000.

Samples of marine life will be taken from the ocean floor by means of dredging and from the water above the disposal sites by midwater trawl operations. Bottom samples will also be used for mineral analysis of rock and clay from the sea floor, and gravity core samples will be used to measure rates of sedimentation and the pos-

sible uptake of radioactive materials by the deposits. A "profile" of water samples will be taken from top to bottom.

A photographic exploration of a sizable portion of the ocean floor at each site will also be made in an effort to obtain pictures both of marine life and of the condition of drums containing the disposed radioactive material.

References

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2. Uranium Hexafluoride: Base Charges, Special Charges, Specifications, and Packaging, AEC Press Release IN-71, Apr. 11, 1960.
3. Domestic Uranium Production Statistics for Last Half of 1959 Announced by AEC, AEC Press Release C-50, Mar. 25, 1960.
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(4): (April 1960).
5. *Reactor Fuel Processing*, 3(2): (April 1960).
6. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(2): (February 1960).
7. AEC Proposes Regulations to Protect Against Criticality and Radiation Exposures During Shipments of Irradiated Fuel Elements, AEC Press Release C-39, Mar. 16, 1960.
8. AEC Formulates Policy for Land Disposal of Radioactive Wastes; Government-Controlled Sites To Be Established As Needed, AEC Press Release C-12, Jan. 28, 1960.
9. AEC Sets Hearing on Coastwise Marine Disposal Co. License, AEC Press Release C-69, Apr. 15, 1960.
10. License Hearing to Resume in New Britain, Conn., AEC Prelease C-46, Mar. 21, 1960.
11. Mines Development Hearing Postponed to March 25, AEC Press Release C-25, Feb. 15, 1960.
12. AEC Contracts for Study of Pacific Waste Disposal Sites, AEC Press Release C-35, Mar. 8, 1960.

Two minor radiation accidents were reported recently: at the Oak Ridge National Laboratory (ORNL) an employee received radiation exposure to the skin above permissible levels during cleanup of a hot cell; and at General Electric Co.'s Vallecitos Atomic Laboratory a technician inhaled an amount of radioactive iodine above permissible levels. Neither man lost any work time, although both are under medical observation.[1] A potentially serious radiation incident occurred at ORNL.

The ORNL accident[2] occurred on April 26 in the Solid States Building in a cell which was being used for examination of an irradiated fuel element. The material was released when a change in the internal air flow in the building carried radioactive material out of the cell in which the irradiated fuel element was being examined. The radioactivity, consisting of graphite containing some fission products, was confined to the building.

Eight persons in the immediate vicinity when radioactive material was released inhaled some contaminated particles. Studies are in progress to determine the extent of internal exposure to these individuals.

After the incident, film badges worn by these individuals indicated a maximum reading of 120 millirads of penetrating radiation. However, this figure represents the total penetrating radiation received since April 1, the date the film badges were last changed. The maximum permissible dosage is 3000 millirads quarterly.

The cleanup of the building has been complicated by some radioactive material which got into the building's air-conditioning system. The air circulation spread the material through the building and its ventilation system.

The time required for cleanup will depend largely on the amount of work required on the air-conditioning system.

The Oak Ridge National Laboratory sampling program to determine the extent of possible exposures to radiation included approximately 250 persons during the first two weeks following the November 20 radiation accident.[3] It was determined that the nine persons who showed sufficient radiation count to require study received a maximum body burden of plutonium of 1 per cent of the maximum permissible burden.[4]

The Thorex Pilot Plant in which the accident occurred, and two other facilities not contaminated — the Metal Recovery Plant and the Multicurie Fission Products Pilot Plant — remain closed pending completion of a review by the Laboratory of operating procedures. Accidents involving radiation also occurred, without harmful exposure of personnel, on Oct. 30 and Nov. 12, 1959. On the subject of the safety review, ORNL Director Alvin M. Weinberg had this to say in his December annual report to employees:

"The alarming frequency of the incidents obliges us to re-examine many of our basic operating procedures and we have halted all high-level radiochemical operations at ORNL. ... Operators are being asked ... to examine each of their operations at the Laboratory until a full review of the whole situation can be made. This review is expected to culminate in a plan worked out by the Chemical Technology, Operations, and Engineering and Mechanical Divisions to increase the degree of containment of all high-level radiochemical operations with a view possibly to imposing on these operations the same degree of containment as is now required of new reactors."

References

1. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(4): (April 1960).
2. Eight Employees at ORNL Checked for Internal Exposure, AEC Press Release No. 706, May 3, 1960.
3. *Reactor Fuel Processing*, 3(2): (April 1960).
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(2): (February 1960).

The multiplicity of fuel alloys and cladding materials and the lack of standardization of element design make difficult the accommodation of power-reactor fuels into existing chemical processing plants. Consequently a number of "head-end" processes, chemical and mechanical, are under consideration to prepare, from the variety of fuels, fuel solutions which are compatible with existing plants. Some of these remove the cladding separately; some put cladding and fuel into a single solution.

Mechanical Processing

Shearing and sawing methods for fuel-element disassembly or for increased charge size to the dissolver are being examined at Hanford Atomic Products Operation (HAPO) and have been discussed in previous Reviews.[1,2] Their recent reports[3-5] indicate that studies of hack sawing have been essentially completed. Three methods of feeding were tested: the mechanical feed of the Marvel saw, the spring feed of the Peerless saw, and the hydraulic feed of the Racine saw (see previous Reviews[1,2] for descriptions of these saws). Principal results of these hacksaw tests are summarized as follows:[3]

1. "Hardware" removal by hack saw is feasible for all the fuels currently scheduled for HAPO processing if (1) the "weld-edge" (two-piece) blade is used, and (2) if hardware is removed from multirod bundles (e.g., Yankee and Dresden) by cutting through thick end plates rather than rod ends. Unsupported rods bend in the cut so that chipped blades and ruptured cladding can result.

2. A minimum blade life of a ton of fuel per blade can be expected, with an average of 3 to 5 tons per blade.

3. Any one of the three saw types can be used for hardware cutoff. Compared to the cheaper Peerless saw, the Racine cuts faster (2 sq in./min versus $\frac{1}{2}$ sq in./min for massive stainless steel) and gives longer blade life (factor of 2 or more). However, the Peerless saw's spring-feed

system is simpler and more easily remotely operable than the Racine saw's hydraulic feed. The Marvel has a relatively complex feed mechanism (compared to the Peerless), and its performance is intermediate between the Racine and Peerless saws.

When hardware is removed by cutting through the end plates, a "wafer" of hardware remains which must be removed to complete fuel disassembly.[3] A portable puller, fabricated from a standard gear puller, was used to strip $\frac{1}{2}$-in.-thick wafers from a 36-rod bundle. A maximum torque of 300 in.-lb ($\frac{1}{2}$-ton pull) was applied to the puller screw for wafer stripping. Tests show that: (1) a manipulator-operated tool can be designed for wafer pulling, (2) pulling forces are not unusual, and (3) wafers should be thick enough so that bending will not occur.

A band saw was used to cut bundles of unsupported rods in order to study its feasibility for hardware cutoff.[4] At low saw speeds (100 ft/min), neither blade breakage nor rod bending occurred. These preliminary studies indicate that the band saw may be capable of cutting unsupported rods without the shimming and/or "potting" steps found necessary with the cold saw and the hack saw.

Other hardware cutoff studies at HAPO included hacksaw cutting on bundles of unsupported rods. Simulated Yankee assemblies, with solid $\frac{3}{8}$-in.-diameter rods, were cut successfully (i.e., without gross rod bending or blade damage) on both the hydraulic and spring-feed hack saws.[5] The latter, however, required a sacrificial backup plate to limit the blade feed rate. Results were sufficiently promising to warrant fabrication of a more exact Yankee prototype from special tubing. Successful rod cutting with the hack saw eliminates the need for using shims and other special devices.

Scouting studies[4,5] on Yankee fuel disassembly showed that a manipulator- (or crane) operated slitting knife can be used to cut the assembly bands (approximately $\frac{3}{64}$ in. thick by $\frac{1}{2}$ in. wide). V-knives of various shapes have been used successfully. Pull forces vary from

150 to 900 lb for $\frac{1}{2}$-in.-wide bands 20 to 50 mils thick.

In the last Review[1] reference was made to underwater shearing of swaged uranium dioxide fuel elements. These studies have been extended to include sintered uranium dioxide.[3] When pellets of sintered uranium dioxide were cut into 1-in. pieces with the hydraulic shear, approximately 2 per cent of the uranium dioxide was dispersed and suspended in the basin water. This is identical with the amount suspended when shearing swaged uranium dioxide rods.

A cluster of 15 Zircaloy-clad swaged uranium dioxide rods was sheared to study the dispersion of uranium dioxide fines in basin fluid. After 120 cuts at a cutting rate of $1\frac{1}{2}$ cuts per minute (130 lb of uranium processed), the suspended uranium concentration 4 in. below the shear blade was 3 g/liter (~200 liters of basin fluid). Tests with a miniature mockup of the shear and shear basin showed that about 97 per cent of the fines suspended by the shearing operation in quiescent basin fluid can be directed into the catch basket by baffles and funnels. Further, an estimated 99.5 per cent of the total uranium dioxide processed in such a baffled area is deposited in the catch basket without the use of auxiliary cleanup systems.

The shear system is currently being modified to permit testing of a scale model of the modified NPF (nonproduction fuel) shear system recently developed. This concept includes: (1) a shear attached to a critically safe feed trough, (2) a critically safe catch bucket for the sheared material, (3) a critically safe sump below the catch bucket equipped with a recirculation pump, (4) a hydroclone in the circulation line for gross particulate cleanup, and (5) a high-efficiency filter for cleanup of the bath at the end of a shear campaign.

Mechanical processing of Sodium Reactor Experiment (SRE) fuel (uranium rods in stainless-steel NaK-bonded tubes) is being studied at ORNL.[6-8] Tests made to evaluate the performance of an auxiliary decladder die showed that the entire length (~8 ft) of an SRE type element can be slit without excessive scoring of the fuel material.[6]

A 36-tube, ferrule-connected, stainless-steel-clad, Mark-I, prototype SRE fuel assembly filled with porcelain was sheared at 1-in. intervals at an average blade velocity[7] of 2 in./sec. Two similarly shaped "concave upward" plane-of-contact blades operating with a

V-bottom anvil in a vertical 150-ton-thrust hydraulic press were used. About 1.5 per cent of the total metal of the prototype appeared as metallic fines passing a diamond-shaped screen with a mesh size of 0.86 by 0.25 in., which represented essentially all the highly worked pieces. A total of 2.6 per cent of the 86.5 g of Nicrobraze per ferrule section in the Mark-I prototype was in these fines. About 0.4 per cent of the Nicrobraze was less than 3 mils in diameter; this size range of Nicrobraze particles (less than the blade separation) would be expected to contribute significantly to blade wear by galling between the blades.

Since NaK is present as a bonding agent between the cladding and the fuel element, it will be exposed to cutting oil and water in mechanical processing. The results of exploratory tests on the reaction when NaK is contacted with water under a mineral oil blanket[8] indicate that a violent hydrogen explosion will not occur and that continuous reaction cannot be sustained unless steam, or some external heat, is used to agitate and increase the solution temperature to above 100°C.

Chemical Dejacketing

An alternative to mechanical dejacketing or complete chemical dissolution of fuel is selective chemical dissolution of fuel jackets and structural components. Another reagent can then dissolve the exposed fuel cores in a second step. The principal jacket materials are aluminum, zirconium or Zircaloy, and stainless steel.

A variety of processes are used for either selective or complete dissolution of fuel alloys and their claddings. These processes have been given an assortment of names. Table III-1 lists the principal reagents and the alloys for which the processes are effective.

Removal of Zirconium and Zircaloy Jackets

Zirconium-clad or Zircaloy-clad fuel elements having either oxide or uranium-niobium-zirconium alloy cores may be dejacketed by the Zirflex process. In studies at HAPO[3-5] the solubility of zirconium in ammonium fluoride solutions at room temperature has been remeasured employing a different method for the determination of free fluoride concentration. In the free fluoride concentration range of most interest

Table III-1   COMMON NAMES OF HEAD-END PROCESSES

Process name	Principal reagents	Alloy dissolved	Process flow-sheet references*
Darex	$2M$ HCl and $5M$ HNO$_3$	Stainless steel	1(1): 5 (February 1958); 2(4): 8 (October 1959)
Zircex	HCl (gas)	Zirconium, Zircaloy	2(2): 7 (April 1959); 2(3): 8−9 (July 1959)
Zirflex	$6M$ NH$_4$F and $0.5M$ NH$_4$NO$_3$	Zirconium, Zircaloy	1(4): 6 (October 1958); 2(1): 7 (January 1959); 2(3): 6 (July 1959); 3(2): 11 (April 1960)
Sulfex	$2M$ to $6M$ H$_2$SO$_4$	Stainless steel	2(1): 8 (January 1959)
Niflex	$2M$ HNO$_3$ and NH$_4$HF$_2$	Stainless steel	
Perflex	$6.5M$ HF and $0.3M$ H$_2$O$_2$	Zirconium, Zircaloy	3(2): 14 (April 1960)
ARCO†	PbCl$_2$ (fused salt) and chlorine	Zirconium, Zircaloy	3(2): 14 (April 1960)

*All references are to issues of *Reactor Fuel Processing*.
†Alloy Reguline Chlorination Oxidation.

(0.3M to 1.3M), the data agree very well with the expression (NH$_4^+$)^3(ZrF$_6^{--}$)(NH$_4$F) = 1.8. The acidities of these solutions were high enough (pH in the range 6 to 7) that the precipitation of hydrolyzed species was avoided. During the dissolution of zirconium in ammonium fluoride– ammonium nitrate solutions, 5 moles of ammonium hydroxide are produced per mole of zirconium dissolved. Only if essentially all the ammonium hydroxide is expelled from the system is the amount of zirconium which is soluble in the cooled decladding solution governed by the expression given above. Furthermore, the dissolution rate of zirconium in these solutions falls off markedly as the ammonium hydroxide concentration increases. The removal of ammonia is, therefore, important to successful dissolution.

A modified Othmer still was used to determine vapor-liquid equilibrium concentrations of ammonia in boiling Zirflex solutions. The mole fraction of ammonia in the overhead increases from about 0.1 to 0.5 as the concentration of free ammonia in the bottoms increases from 0.1M to 3M.

A procedure in which the ammonia is neutralized with hydrofluoric acid as it is produced is under consideration as an alternative to removing ammonia from the solution.[4] In this process the initial dissolver solution would be 1M ammonium fluoride–0.5M ammonium nitrate. (Dissolution rates for oxide-free Zircaloy-2 in this solution decreased from 22 to 0.35 mils/hr as the pH was increased from 6.8 to 8.9 by

adding ammonia.) As Zircaloy-2 was dissolved at the boiling point, hydrofluoric acid was added to maintain a constant pH of 7. Dissolution rates were generally lower than those obtained in the standard Zirflex decladding procedure (initially 6M ammonium fluoride). An integrated penetration rate of about 10 mils/hr for dissolution to a terminal ammonium fluozirconate concentration of 0.8M was indicated for oxide-free Zircaloy-2.

Zircaloy-2 tubing (55-mil) was dissolved in a pilot plant in Zirflex dissolvent with initial concentrations of 4.8M ammonium fluoride– 0.45M ammonium nitrate and a fluoride-to-zirconium mole charge ratio of 7. A water boil-off rate of 0.132 lb-mole/(hr)(sq ft) was maintained throughout the reaction for the removal of ammonia. A maximum dissolution rate of 23 mils/hr was attained. By comparison, a maximum dissolution rate of 70 mils/hr has been demonstrated in the laboratory for the same initial conditions of the dissolvent. The discrepancy may be attributed to the ammonia effect since much higher boil-off rates and hence more efficient ammonia removal could be accomplished in laboratory runs.

This same Zircaloy-2 tubing in a dissolvent with initial concentrations of 5.5M ammonium fluoride–0.5M ammonium nitrate and a fluoride-to-zirconium mole charge ratio of 7 was dissolved with an average recirculation rate of 16 gal/min and a water boil-off rate of 0.267 lb-mole/(hr)(sq ft). A maximum dissolution rate of 35 mils/hr was attained compared to a labo-

ratory rate of 80 mils/hr, the difference in rates again attributed to ammonia buildup in the pilot-plant dissolvent. This experiment was repeated using a superheated steam (350°F) sparge for solution recirculation. A steam sparge of 2.77 lb/min provided a recirculation rate of 8 gal/min and a boil-off rate approximately equal to the sparge rate, 0.25 lb-mole/(hr)(sq ft). A maximum dissolution rate of 41 mils/hr and an integrated rate of 18 mils/hr were attained.

Recent work[3] has shown the solubility of U(IV) in ammonium fluoride solutions at room temperature to be lower at low ammonium fluoride concentrations than was previously reported.[2] In this work greater care was taken to exclude air, which can oxidize U(IV) to the more highly soluble U(VI), and the concentrations of U(IV) were determined spectrophotometrically. These data indicate the room-temperature solubility of U(IV) in $1M$ ammonium fluoride is about $0.0004M$ and about $0.0001M$ in $0.5M$ ammonium fluoride. These values indicate that the loss of U(IV) to the cooled decladding solution will be less than 0.1 per cent.

This quarter's modifications of Zirflex at ORNL include adaptation of the general scheme to accommodate 1 to 10 per cent uranium-zirconium alloys.[9]

In hot-cell Zirflex decladding experiments with unirradiated samples and pressurized-water reactor (PWR) fuel specimens irradiated to 1950 Mwd per ton of uranium,[7] soluble uranium losses were 0.01 and 0.11 per cent and plutonium losses were 0.05 and 0.08 per cent, respectively. The soluble uranium losses compare favorably with experimental values on unirradiated fuel samples previously reported by other groups. The main difficulty in the flow sheet appears to be precipitation in the diluted waste solutions.

The solubility of zirconium fluoride in nitric acid–ammonium fluoride solutions was determined at 25°C. In solutions where the fluoride-to-zirconium mole ratio was greater than about 8, the solubility decreased with increasing nitric acid concentration. Since the solubility was greater in the presence of nitric acid when the fluoride-to-zirconium ratio was between 6 and 8, no deleterious effect is expected if a Zirflex decladding solution should be contaminated with a trace of nitric acid.

In a series of cyclic Zirflex decladding-dissolution runs on unirradiated prototype PWR fuel pins[8] (Zircaloy-2-clad uranium dioxide),

the amount of solids found in filtered decladding waste and product solutions increased with the number of cycles. The $ZrO_2 \cdot 2H_2O$ in the decladding solutions probably was formed when ammonium hydroxide was returned to the dissolver from the updraft condenser. Stannic oxide was the chief component of the solids in the core solutions. A gradual increase in pore size of the glass filter used in these tests may be responsible for the appearance of increasing amounts of solids as the number of cycles increased.

Removal of Stainless-Steel Jackets

Parallel flow sheets have been developed at ORNL[10] for Consolidated Edison power-reactor fuel using boiling $6M$ sulfuric acid (Sulfex) or dilute aqua regia (Darex). These two flow sheets are given in Fig. 1. The Darex dissolver is titanium and the Sulfex, Nionel.

Two modifications of the Sulfex process were tested: (1) decladding with 200 per cent excess of $6M$ sulfuric acid, and (2) initiating the reaction with $6M$ sulfuric acid and diluting to $4M$ sulfate shortly thereafter. Uranium losses to the decladding solution were generally between 0.2 and 0.5 per cent but were as high as 0.9 per cent in the presence of a ThO_2-U_3O_8 heel. The uranium losses were directly related to the amount of heel present. In most cases the fuel pins were passive to boiling $6M$ sulfuric acid, and reaction was initiated by contacting the pin with a piece of iron. Core dissolution was less efficient than in the Darex tests, presumably because of sulfate contamination. Under the flow-sheet conditions, only 98 to 99 per cent of the core was dissolved in each cycle.

Engineering-scale studies on several fuels indicated that Sulfex dissolution rates for tubular-clad elements are only one-half to two-thirds of those expected from earlier data obtained on plates.[6,7]

In cyclic Sulfex depassivation tests, stainless-steel corrosion rates were 10.7 and 4.4 mils/month for three cycles when $10M$ and $8M$ sulfuric acid, respectively, were substituted for $12M$ sulfuric acid in the initial 5 min of the cycle. The corresponding rate for $12M$ sulfuric acid is at least 80 mils/month (27 mils per 100 cycles).

The Sulfex process is also being studied at HAPO[5] and Battelle Memorial Institute.[11] The use of boron (boric acid) as a soluble neutron
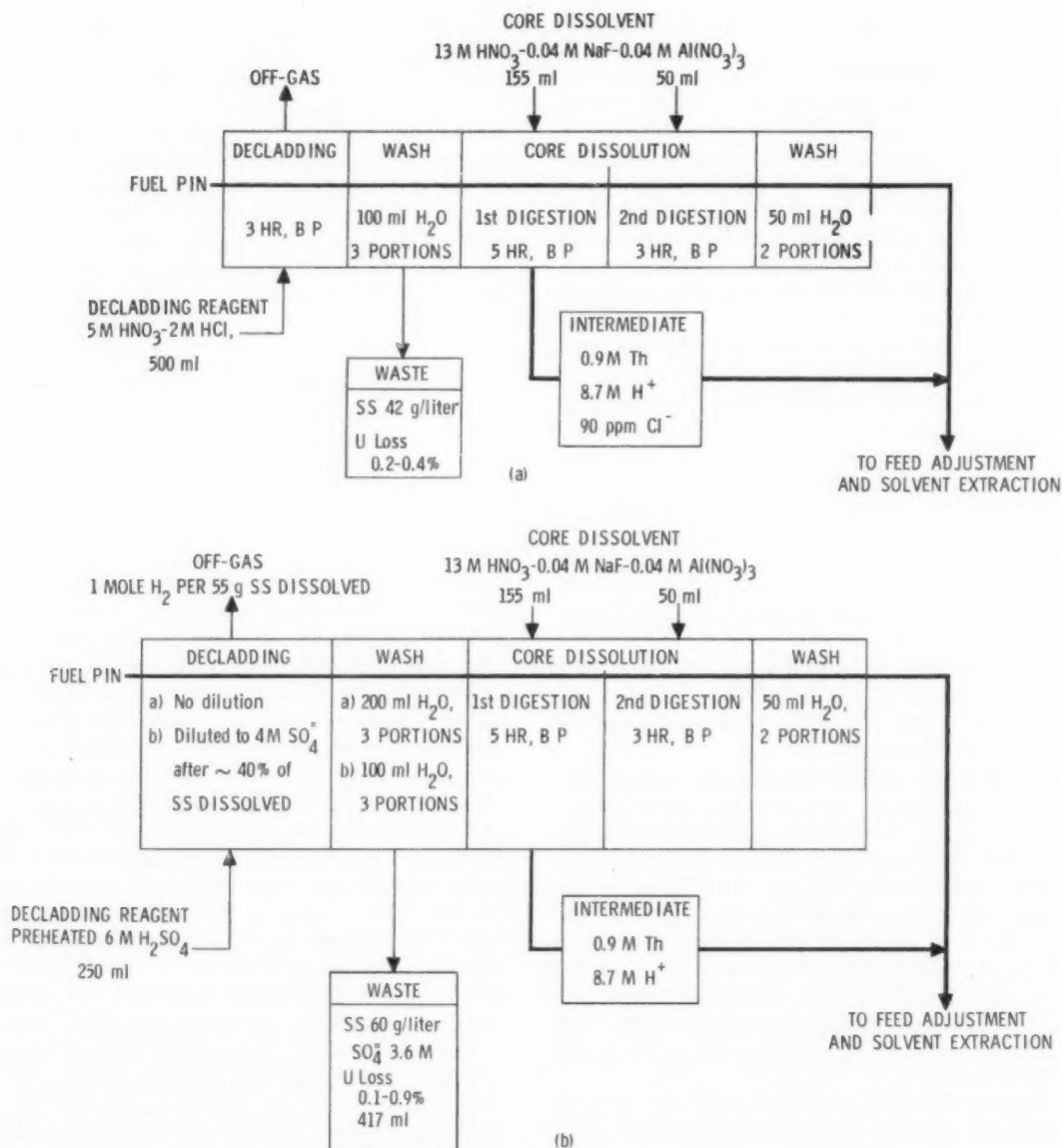
Figure 1—Flow sheets for (a) Darex and (b) Sulfex decladding of Consolidated Edison fuel elements.[10]

poison during Sulfex decladding is being explored.[5] At room temperature the solubility of boric acid in $4M$ to $6M$ sulfuric acid is about $0.3M$. Dissolution rates for 304L stainless steel were not appreciably affected by the presence of $0.3M$ boric acid, and no effect of boric acid on uranium dioxide core losses was noted.

Two bench-scale Sulfex dissolution runs were made at HAPO[4] using the technique of starting

the dissolution in $4M$ sulfuric acid and then diluting the decladding solution to $2M$ sulfuric acid. Average penetration rates for the runs were 3 to 6 mils/hr, about fourfold lower than those obtained in $4M$ sulfuric acid.

Losses of fertile and fissile materials during chemical decladding of irradiated prototype Consolidated Edison power-reactor fuel pins by the Sulfex and Darex processes were deter-
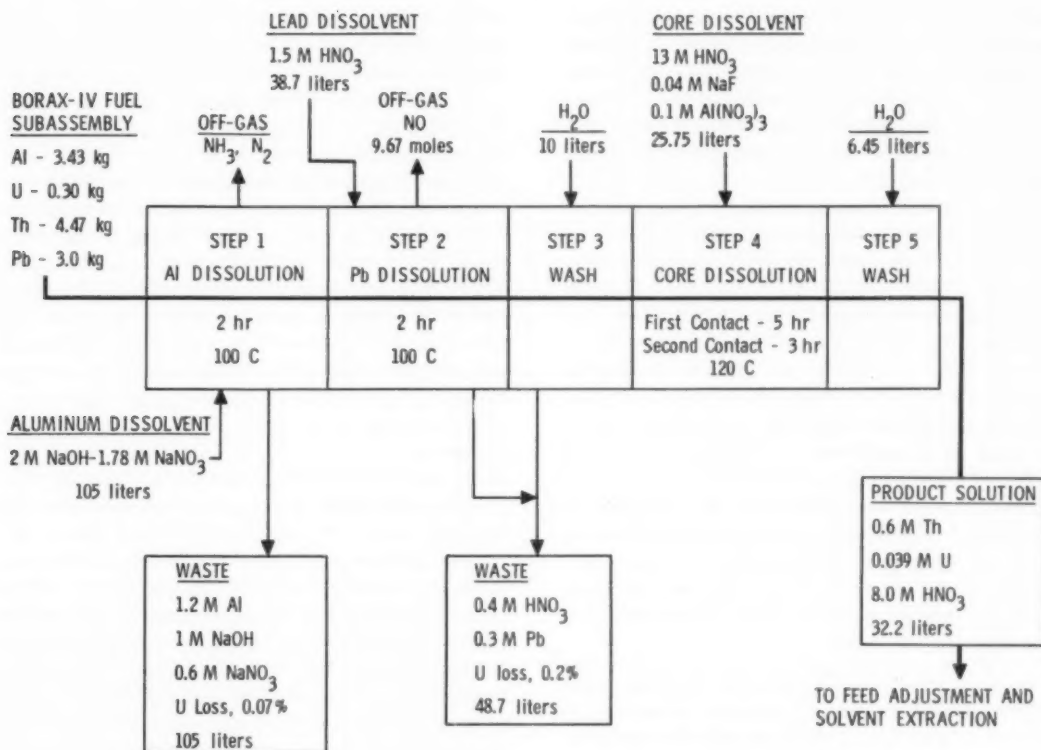
Figure 2—Flow sheet for the two-step dissolution of BORAX-IV fuel.[12]

mined, on a laboratory scale, in an all-glass apparatus.[11] For air-fired low-density (~85 per cent of theoretical) fuel cores, minimum losses of uranium, thorium, and plutonium were in the 0.1 to 0.2 per cent range, by either process. These losses increased if the dejacketed cores were allowed to remain in contact with the cladding solution. No selectivity of dissolution of core components was apparent. Comparable losses were obtained with similar unirradiated fuel pins.

Irradiated core pellets showed a tendency to shatter. When shattered core pellets were present, losses to the cladding solution were excessive (0.5 to 4.5 per cent). No correlation between burnup and extent of shattering was discernible.

Removal of Aluminum Jackets

The BORAX-IV reactor fuel consists of 6.35 per cent $UO_{2.3}$-ThO_2 pellets encased in 1 per cent nickel—aluminum alloy and bonded with lead. In the preferred process for dissolution,[12] the aluminum is dissolved first in boiling $2M$ sodium hydroxide—$1.78M$ sodium nitrate with a uranium loss of ~0.07 per cent. The lead and nickel are then dissolved in boiling $1.5M$ aluminum nitrate with uranium losses of <0.2 per cent (see Fig. 2 for flow sheet).

Dissolution

Simultaneous Dissolution of Jacket and Core

Zirconium Fuel Elements. Studies of dissolution of zirconium-uranium alloy scrap have been made at the Y-12 Plant. Zirconium-uranium alloys containing up to 20 per cent uranium can be rapidly and completely dissolved in aqueous hydrofluoric acid with the addition of a small amount of nitric acid near the end of the reaction.[13] Zirconium-uranium alloys containing less than 20 per cent zirconium may be dissolved in nitric acid containing a small quantity of hydrofluoric acid for complexing the zirco-

nium. This dissolution may be carried out in stainless-steel equipment if aluminum nitrate is added to complex the original hydrofluoric acid. The addition of sufficient aluminum nitrate to increase the specific gravity to 1.36 provides a solution suitable for solvent extraction with dibutyl carbitol.

In a proposed procedure for total dissolution of Zircaloy-2-clad uranium dioxide fuels, the Zircaloy-2 is removed by the Zirflex process. Uranium dioxide cores are then dissolved by adding nitric acid and aluminum nitrate to the decladding solution. In development studies on this procedure, dissolution rates for uranium dioxide were determined in diluted terminal Zirflex decladding solutions, $0.6M$ $(NH_4)_2ZrF_6$, adjusted to nitric acid concentrations from $0.75M$ to $1.5M$ and to mole ratios of aluminum to free fluoride from zero to 1.25. Dissolution rates were relatively low and ranged from about 60 down to about 6 mg/(hr)(cm^2). As expected, the rates decreased as nitric acid concentration decreased and as the mole ratio of aluminum to free fluoride increased.

Stainless-Steel Fuel Elements. In flow-sheet studies for N.S. *Savannah* fuel processing,[7] stainless-steel-clad uranium dioxide pellets, irradiated to 7490 and 12,400 Mwd/ton, were dissolved in hot-cell tests in $5M$ nitric acid—$2M$ hydrofluoric acid; the chloride was removed to final concentrations of 490 and 160 ppm, respectively.

Dissolution of Dejacketed Material

Dissolution of the core is possible if fuel jackets can be removed mechanically or physically, or dissolution may be performed when the fuel is sheared into pieces. Consequently, a simpler dissolution procedure may be possible than when combined jacket-core dissolution is carried out.

At HAPO the dissolution of uranium-molybdenum alloy fuel cores is being studied;[3] one method utilizes nitric acid—Fe(III) nitrate solutions, whereas the other incorporates strong nitric acid dissolutions. During dissolution of uranium—3 wt.% molybdenum—0.2 wt.% silicon and uranium—3 wt.% molybdenum—0.2 wt.% aluminum alloys in solutions initially $12M$ to $14M$ nitric acid to yield dissolver solutions $1.0M$ to $1.5M$ UO_2^{++} and $4M$ to $8M$ nitric acid, most (85 to 90 per cent) of the molybdenum precipitates as a white solid. X-ray diffraction

analyses indicate the solid to be orthorhombic Mo(VI) oxide. About 90 per cent of the silicon from the uranium-molybdenum-silicon alloy is also precipitated under these conditions. Precipitation of both molybdenum and silicon is more complete (about 95 per cent) if the slurries are digested at boiling after dissolution is complete. The molybdenum oxide precipitate does not settle well but centrifuges to about 10 vol.% from $1.5M$ UO_2^{++} solutions. Most of the uranium and plutonium associated with the solid can be removed by washing with water or dilute nitric acid. However, after exhaustive washing with water, dilute nitric acid, and dilute sodium dichromate, the solids (washed and oven dried) contain about 0.06 wt.% of both uranium and plutonium (2.5 per cent of plutonium retained).[4] This could represent a significant loss of plutonium, depending on the irradiation history of the fuel.

Head-end processes for uranium-molybdenum fuels are also being examined at ORNL.[7] It is planned that the stainless-steel-clad NaK-bonded uranium-molybdenum Power Reactor Development Company (PRDC) blanket and Consumers Public Power District (CPPD) fuel will be mechanically declad and the NaK destroyed with steam prior to dissolution of the uranium-molybdenum alloy. In uranium-molybdenum dissolution and feed preparation studies, the solubility of $MoO_3 \cdot 2H_2O$ in $2M$ to $5M$ nitric acid at 26°C decreased with increasing uranyl nitrate concentration. For example, in solutions containing $3M$ nitric acid, the molybdenum concentration decreased from $0.12M$ to $0.08M$ as the uranium concentration increased from zero to $0.95M$. These data indicate that molybdenum will not precipitate during solvent extraction of nitric acid solutions of uranium and molybdenum, from which $MoO_3 \cdot 2H_2O$ has been removed by prior centrifugation.

Studies are being made at ORNL of the recovery of uranium and thorium from graphite fuels.[6] Two samples of graphitized reactor fuel were disintegrated to −20 mesh in 1.5 hr at ambient temperature by immersion in 90 per cent fuming nitric acid containing a maximum of 0.2 per cent dissolved oxides. The resulting powders were leached in boiling 90 per cent nitric acid. Similar samples were ground to −4 +8 mesh and leached with boiling $15.8M$ nitric acid. The uranium recovery from the first material (0.7 per cent uranium in graphite) was 94 per cent with the 90 per cent fuming nitric

acid versus 80 per cent with the 15.8M nitric acid. The uranium and thorium recoveries from the second samples (1.5 per cent uranium and 7 per cent thorium in graphite) were 99 per cent and 93 per cent, respectively, in 90 per cent fuming nitric acid versus 90 per cent of the uranium with 15.8M nitric acid. The use of 90 per cent nitric acid for disintegrating and leaching of graphite fuels may be a practical alternative to grinding and leaching.

Minus 20-mesh powder was also obtained from 0.7 per cent uranium in graphite samples by refluxing in iodine monochloride (ICl) or iodine monobromide (IBr).[5,6] In two subsequent leaches of the disintegrated sample in boiling 15.8M nitric acid, uranium recoveries were 96 and 99 per cent.

Graphitized fuel specimens containing 0.7 and 5 per cent uranium were disintegrated (to −20 mesh) and then leached in boiling 90 per cent nitric acid for 4 hr.[7] After washing and a second nitric acid leach, the uranium recovery was 99.85 per cent from the 5 per cent fuel and 97 per cent from the 0.7 per cent fuel. With mechanical grinding to −16 +30 mesh and leaching twice with boiling 15.8M nitric acid, uranium recoveries were 99.85 and 83 per cent, respectively, for the two fuels.

The 90 per cent acid attacked Pebble Bed Reactor prototype 1.5-in.-diameter balls containing 10 per cent high-fired uranium dioxide mixed with graphite at a much lower rate.[7] A 2-hr contact at 25°C, followed by 4 hr in boiling 90 per cent nitric acid, washing, and a second 4-hr reflux in 90 per cent nitric acid, disintegrated 80 per cent of a graphitized specimen for a uranium recovery of 87 per cent. Only 41 per cent of an ungraphitized sample was disintegrated; the amount of uranium recovered was 62 per cent. Increasing the contact time to 32 hr resulted in 93 per cent of the ungraphitized material being disintegrated; metal recovery was 95 per cent.

Uranium and thorium recoveries were >99 per cent when −10-mesh samples of prototype ungraphitized Pebble Bed Reactor fuel were leached with boiling 13M nitric acid−0.04 sodium fluoride−0.1M aluminum nitrate, as compared to 7 per cent thorium recovery with 15.8M nitric acid.[7]

Aluminum tubes were dissolved in the "flooded tray" dissolver at HAPO[3] with mercuric-nitrate-catalyzed nitric acid in 19 recirculator runs and in 12 laboratory batch runs. At average recir-

culation rates of only 0.2 gal/(hr)(sq ft of charge), the recirculator dissolution rates were about one-fifth of the batch rates. Peak dissolution rates were 500 mils/hr with 5.5M nitric acid−0.005M mercuric nitrate in the batch runs and about 80 mils/hr with 7.0M nitric acid−0.005M mercuric nitrate in recirculating runs.

One uranium−3 wt.% molybdenum dissolution was made in the flooded-tray dissolver.[5] This run, simulating initial Piqua reactor fuel core dissolving conditions of 1.25M nitric acid−1M Fe^{+3}, gave an attack rate of about 60 mils/hr, as compared to 40 mils/hr that would be predicted from laboratory data.

In the case of BORAX-IV reactor fuel, after the cladding and bonding are removed, the oxide core (6.35 per cent $UO_{2.3}$-ThO_2) is dissolved in two successive digestions with boiling 13M nitric acid−0.04 M sodium fluoride−0.1M aluminum nitrate to produce a solution 0.6M in thorium and 0.04M in uranium.[12]

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Solvent Extraction

Modifications of the Purex Process

Purex processing, currently used both in this country and abroad for the recovery of most irradiated fuels, employs an extractant of tributyl phosphate (TBP). Although first routine production operation of the Purex process at the Hanford Atomic Products Operation (HAPO) was begun in 1956, four years of operating experience with TBP as the solvent had been obtained earlier via the operation of the extensive waste metal recovery program. The Purex process was operated at the Savannah River Laboratory in about 1954. Many improvements in the original process have been made as a result of in-plant and laboratory development programs and the prolonged manufacturing experience with TBP as a solvent for uranium and plutonium.[1]

A modification of the Purex process, the Thorex process, is used for the recovery of uranium and thorium from irradiated fuels. The standard Thorex process employs aluminum nitrate salting agent to avoid the use of high acid conditions which lead to third-phase formation. A process which does not require a salt is desirable because the aqueous waste-disposal problem would be simpler. In a previous Review[2] it was mentioned that preliminary laboratory tests showed that the use of Decalin instead of kerosene as the Purex diluent provided greater solubility for the thorium-TBP complex and could accommodate a high acid environment. Thus the Decalin diluent eliminated the need for aluminum nitrate salting. However, further studies have shown Decalin to be unsatisfactory because it provides very poor decontamination from ruthenium.[3]

Another approach to the problem of eliminating aluminum nitrate from the Thorex process involves the injection of concentrated nitric acid into an appropriate extraction stage.[3] In this procedure, which has been demonstrated on a laboratory scale, the feed solution was $0.1N$ acid deficient, the scrub solution was $2M$ in

nitric acid, and $13M$ nitric acid was injected in the fourth extraction stage. The laboratory contactor consisted of five extraction and six scrub stages, and the extractant was 30 per cent TBP in kerosene. Decontamination factors realized were 200, 8000, and 900 for ruthenium, zirconium-niobium, and protactinium, respectively. These values are as good as those realized under the standard Thorex flow sheet.

A Purex type process has been developed for separation and recovery of promethium from mixed fission-product rare earths.[4] Single-stage separations factors of 1.9 were realized between successive elements by extraction with 100 per cent TBP from $12N$ nitric acid solution. The distribution coefficients for neodymium, promethium, and samarium were 0.43, 0.82, and 1.55, respectively.

The separation of promethium from mixed rare earths was accomplished in a two-cycle process. In the first cycle, promethium was separated from neodymium and lighter elements, and, in the second cycle, samarium and heavier elements were removed. It was estimated that from a typical mixture of fission-product rare earths a 90 per cent yield of 83 per cent pure promethium could be obtained.

Studies of Alternate Extractants

Considerable attention has been devoted to the investigation of a number of organonitrogen and organophosphorus compounds in solvent-extraction separation processes. Certain of these compounds are superior to TBP in extraction power, selectivity, and adaptability to acid media other than nitric acid.

Fluorination-plant residues contain significant quantities of uranium and small amounts of technetium and neptunium. Currently, these values are recovered from leach solutions by TBP extraction. A more efficient and more versatile process based on extraction with trilaurylamine (TLA) has been demonstrated on a laboratory scale.[5] Technetium(VII) and neptunium(IV) were coextracted with $0.3M$ TLA.

Neptunium was partitioned with $0.1N$ sulfuric acid, and technetium was stripped with $1N$ ammonium hydroxide. Using an extractant of $0.3M$ TLA in kerosene modified with 2 vol.% tridecanol, uranium could either be retained in the aqueous phase at low nitrate concentrations or coextracted at higher nitrate concentrations.

Studies of the synergistic effect of combinations of acid and neutral extractants continue. Table IV-1 shows recent data demonstrating the effect realized by an equimolar combination of

Table IV-1   SYNERGISTIC EFFECT OF COMBINATION OF DNNSA AND DAAP*[6]

(Aqueous Phase Initially $1M$ in Uranium)

Extractant* in kerosene	Initial aqueous pH	Sulfate concentration, M	E_a^o for U(VI)
$0.1M$ DNNSA	1.0	0.5	0.22
	1.8	0.5	0.21
$0.1M$ DAAP	1.0	0.5	0.09
	1.8	0.5	0.23
$0.1M$ DNNSA }	1.0	0.5	125
$0.1M$ DAAP }	1.8	0.5	150

*DAAP = diamylamyl phosphonate.
 DNNSA = dinonylnaphthalene sulfonic acid.

Table IV-2   COMPARISON OF EXTRACTION POWER OF DIALKYL PHOSPHORIC ACIDS[6]

$0.1M$ dialkyl phosphoric acid* in kerosene	E_a^o for U from aqueous solution $0.4M$ PO_4^{---} (pH 1) and $0.004M$ U(VI)
DBEPA	1000
D-n-o-PA	80
DTMHPA	50
D2EHPA	25

*DBEPA = di(β-butoxyethyl) phosphoric acid.
 D-n-o-PA = di(n-octyl) phosphoric acid.
 DTMHPA = di(3,5,5-trimethylhexyl) phosphoric acid.
 D2EHPA = di-2-ethylhexyl phosphoric acid.

$0.1M$ diamylamyl phosphonate (DAAP) and $0.1M$ dinonylnaphthalene sulfonic acid (DNNSA).[6] The data presented are for sulfate systems and show an improvement in the extraction coefficient by a factor of 500. In nitrate systems, significant, but slightly lower, improvement was noted. With tests of TBP as the neutral reagent, $0.1M$ TBP and $0.05M$ DNNSA, a much smaller increase in the distribution coefficient by a factor of 14 was noted.

Other tests showed di(β-butoxyethyl) phosphoric acid (DBEPA) to be the most powerful uranium extractant of all dialkyl phosphoric acids examined to date.[6] Considerable process development work has been based on di-2-ethylhexyl phosphoric acid (D2EHPA). In kerosene diluent, DBEPA was 17 to 40 times more effective than D2EHPA, and, in carbon tetrachloride diluent, it was 100 to 160 times more effective than D2EHPA. Several dialkyl phosphoric acids are compared in Table IV-2.

Di-n-butylphenyl phosphonate (D-n-BPP) and di-sec-butylphenyl phosphonate (D-s-BPP) were found to be better uranium extractants than TBP and to possess greater resistance to radiation damage.[6] However, the uranium complexes formed were relatively insoluble in a kerosene diluent.

The previous Review[7] discussed the recovery of strontium from Purex waste. Experimental data now available show that over 99 per cent of the strontium can be recovered from Purex waste with less than 3.6 per cent of the iron by extraction with D2EHPA.[8] The feasibility of separating alkaline-earth elements with D2EHPA was demonstrated, and distribution coefficients of 493, 52, and 0.1 were obtained for calcium, strontium, and barium, respectively.

Solvent Degradation

The search continues for a superior Purex diluent. In addition to acceptable chemical and physical properties with respect to density, flammability, chemical resistance, and solvent properties, the preferred diluent must show superior resistance to radiation damage. At the present time Amsco 125-82, a kerosene fraction, is the diluent employed in most Purex processing.

Tests of Solvesso-100 revealed superior resistance to radiation damage as compared to Amsco 125-82 (reference 9). Solvesso-100 is a high aromatic hydrocarbon with a flashpoint of $118°F$. As shown in Table IV-3, the acid yield on irradiation was lower by a factor of 3 for TBP diluted with Solvesso-100. Di-sec-butylphenyl phosphonate acid yields were low and showed no significant effect of the diluent. It was observed that the phenyl group, which appears both in D-s-BPP and Solvesso-100, may contribute to the radiation resistance of the solvent.

Table IV-3 RADIOLYSIS ACID YIELD FROM
EXTRACTANTS DILUTED WITH AMSCO 125-82
AND SOLVESSO-100[9]

Extractant[*]	Diluent	Acid yield, moles per 100 ev
1M TBP	Amsco 125-82	0.81
1M TBP	Solvesso-100	0.28
1M D-s-BPP	Amsco 125-82	0.22
1M D-s-BPP	Solvesso-100	0.19

[*]D-s-BPP = di-sec-butylphenyl phosphonate.
TBP = tributyl phosphate.

Fundamental Solvent-Extraction Studies

The fact that TBP will extract uranium from
various acid media is known and is being ex-
ploited in production facilities. The fundamental
mechanisms and reaction kinetics involved are
still being debated and continue to be of theoreti-
cal interest. In the previous Review[7] the work
of an Idaho group on the transfer of uranium
across an interface was discussed. Work along
similar lines at Hanford and Fernald is noted
herein.

The Hanford workers sought to study the
transfer of uranium from an organic phase (TBP
in kerosene) into an aqueous phase across a
fixed, stable interface.[10] Consideration was
given to a host of variables including stirring
rates in the bulk phases, direction of transfer,
presence or absence of surface-active agents,
and temperature. With respect to the transfer
mechanisms, organic-to-aqueous transfer was
first order with respect to uranium concentra-
tion, independent of TBP concentration, and
nearly independent of aqueous-phase stirring.
Data obtained for aqueous-to-organic transfer
could not be fitted to a conventional rate equa-
tion. It was concluded that factors not measura-
ble in the bulk phases frequently controlled
transfer rates, and spontaneous interfacial tur-
bulence was submitted as a likely candidate.

The Fernald workers pursued an applied pro-
gram to determine the effect on uranium parti-
tion between TBP and an aqueous solution of
various reagents added to the aqueous phase.[11]
Prior work by this group of a related nature
was discussed in an earlier Review.[12] This work
clearly shows that uranium extraction by TBP
is benefited more by nitrate salts in combination
with a minimum quantity of nitric acid than by
nitric acid alone. This effect is illustrated in
Fig. 3. Actually the salting effect is not new

knowledge, although it has perhaps not previ-
ously been the subject of so exhaustive a study.

Other findings of the Fernald study indicate
that the principal role of nitric acid is con-
sidered to be that of enabling formation of the
extractable neutral uranyl nitrate. It was dem-
onstrated experimentally that the optimum ura-
nium partition depended on a balance between
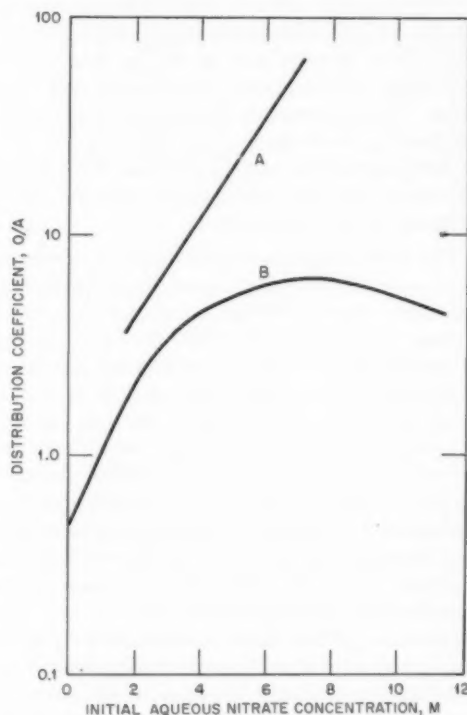hydrogen and nitrate ions.

Figure 3—Comparison of uranium partition into TBP
from aqueous solutions containing nitric acid and
nitric acid—sodium nitrate.[11] Curve A, sodium nitrate
added to 1M HNO$_3$. Curve B, HNO$_3$.

Precipitation Processes

A knowledge of the chemistry of protactinium
is of importance in connection with the chemical
processing of irradiated thorium, where Pa^{233}
is an intermediate in the production of fissile
U^{233}. Protactinium-231, an alpha emitter with a
half life of about 3.4×10^4 years, is the longest-
lived isotope of protactinium and, as such,
is the most suitable for chemical studies.

Protactinium-231 occurs naturally in uranium ores to the extent of about 0.2 to 0.3 ppm of the amount of uranium present. During refining of the ores, protactinium distributes itself among the various waste streams of the refinery process. In Great Britain, process development studies were carried out to recover protactinium from the ethereal sludge which had been accumulated from an earlier uranium concentration process at the Springfields refinery.[13]

The process chosen involves leaching the sludge with $4N$ nitric acid containing $0.1M$ fluoride. Over 95 per cent of the protactinium is extracted together with 99 per cent of the uranium. The presence of fluoride is essential for efficient protactinium recovery. The uranium is then extracted with 20 per cent TBP solvent and recovered by conventional methods. Protactinium is not extracted.

The most widely used technique for recovering low concentrations of protactinium from solution has been that involving carrier precipitation. Almost any precipitate will carry protactinium to some extent. It was found that the addition of aluminum chloride directly to the leach raffinate gives rise to a precipitate in the cold that carries down most of the protactinium. The precipitate, consisting of hydrous oxides and phosphates of impurities (mainly zirconium) in the raffinate, is thought to result from hydrolysis and phosphate formation following the release of impurities from fluoride complexes by the competitive action of the aluminum.

The precipitate, after metathesis with caustic soda, can be redissolved in hydrochloric acid ($8N$), giving a stable solution of protactinium. This solution is heavily contaminated with iron and zirconium. Final purification of the protactinium is accomplished with di-isobutyl ketone and stripping from the solvent with $8N$ hydrochloric acid containing $0.1M$ fluoride.

In a final laboratory test the process showed an over-all protactinium recovery of 68 per cent. A product of about 95 per cent chemical purity is attainable.

Ion-Exchange Processes

Recovery and Purification of Americium, Curium, and Promethium

Americium may be recovered with good yield and at high purity from a nitric acid feed material containing as little as 1 mg of americium per liter, together with gross amounts of lanthanum, iron, plutonium, aluminum, and other elements by the following ion-exchange procedure[14] (see Fig. 4):

1. Plutonium is removed by sorption onto an ion-exchange resin (Dowex 1) in a $7M$ nitric acid system.

2. Transition from a nitric acid system to an ammonium thiocyanate system is then made by adjusting the nitric acid solution to proper ionic strength, loading a cation-exchanger resin (Dowex 50), and subsequently eluting the resin with $5M$ ammonium thiocyanate. By employing a dilute thiocyanate wash prior to elution, a major part of the iron impurity may be removed.

3. Major separation of americium from impurities is obtained in the $5M$ thiocyanate system by loading the thiocyanate complexes onto an anion-exchange resin (Dowex 1), washing the column free of impurities including the rare earths with additional $5M$ ammonium thiocyanate, and finally eluting the americium from the resin with $0.1M$ hydrochloric acid. This eluate will contain all the americium and plutonium which were sorbed on the resin, plus some aluminum if aluminum was originally present, and small amounts of iron.

4. To obtain final purification of the product, the $0.1M$ hydrochloric acid eluate from the thiocyanate column is dripped into a strong base. Amphoteric aluminum remains in solution while americium, plutonium, and iron are precipitated. This precipitate is washed and then dissolved in $7M$ hydrochloric acid. The plutonium and iron are then fixed on anion-exchange resin (Dowex 1), and the purified americium solution is obtained by washing the resin column with additional $7M$ hydrochloric acid.

Development of anion-exchange procedures for separating actinides and lanthanides continued at ORNL.[8] Americium was satisfactorily separated from synthetic feed solutions containing macro amounts of mixed rare earths and tracer americium. Seven grams of americium—rare earths per liter of resin was loaded on a 40-cm column of Dowex 1-8X (50 to 100 mesh) resin from $8M$ lithium nitrate at 80°C. The sorbed rare earths were completely eluted in 5 to 8 column volumes of $10M$ lithium chloride at 80°C, and americium was eluted in 2 column volumes of $1M$ lithium chloride at 80°C. The
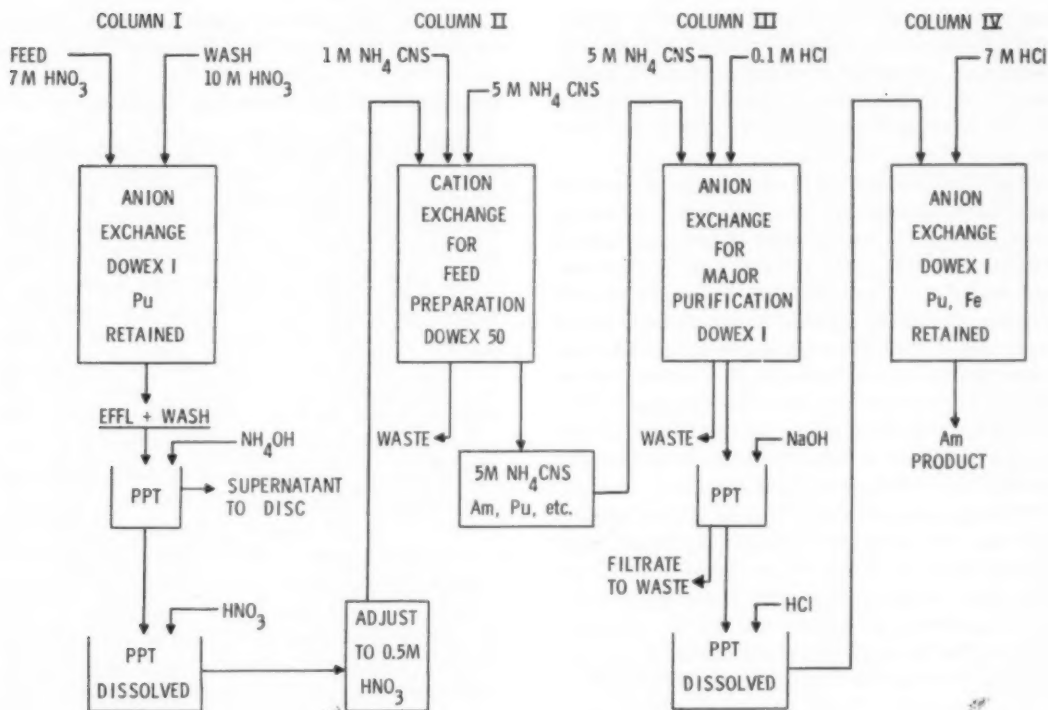
Figure 4 — Flow sheet for americium recovery.[11]

product contained 99.9 per cent of the americium and no detectable rare earths. Attempts to use shorter columns were not successful; for example, a 20-cm column gave a product which was free of rare earths but which contained only 85 to 90 per cent of the americium.

A modification of this procedure was used to recover Am^{241} and Cm^{242} from 1 mg of irradiated Am^{241}. For this purification, the anion-exchange column was loaded using $12M$ lithium chloride instead of $8M$ lithium nitrate. The product contained 98 per cent of the americium-curium and was decontaminated from rare-earth fission products by a factor of more than 100 and from gross beta activity by a factor of 20. Zirconium-niobium, which behaved in the same manner as americium-curium, was the only major contaminant. Additional purification was obtained by sorbing americium and curium on Dowex 50W-10X (100 to 200 mesh) resin and eluting with $0.4M$ ammonium α-hydroxy isobutyrate, pH 4.15 at $85°C$. Since zirconium-niobium did not sorb on the resin, an additional beta decontamination factor of 75 was obtained.

Equilibrium studies for determining distribution coefficients at a tracer level, and elution curves based on analyses of fractions of eluates from anion- and cation-exchange processes at activity levels from 1 to 75 curies, established conditions for the purification of promethium from the other inactive and long-lived radioactive rare earths and from americium produced during fission of U^{235} (reference 15).

Promethium is purified from fission-produced rare earths by cation exchange by using $0.2M$ citrate, $0.25M$ lactate, or $0.5M$ α-hydroxy isobutyrate. A comparison of the efficiencies of the three eluants may be expressed in the following manner: α-hydroxy isobutyrate > lactate > citrate.[15]

Promethium is separated from americium by adsorbing both the americium and the promethium thiocyanate complexes on Dowex 1 resin and by eluting promethium with $5.0M$ to $6.0M$ ammonium thiocyanate solution. Americium remains on the ion-exchange column to be desorbed with $0.1N$ HCl solution.

Radiation damage to resins and solutions is not expected to present difficulty when the proc-

ess expands to 1000- to 5000-curie levels. Small resin columns were operated with the top portion of the column saturated with 75 to 100 curies of radioactivity. Calculated separation factors were as expected from equilibrium studies.

The rare earths cerium through europium may be separated from each other by elution from Dowex 1 resin with $6.0M$ ammonium thiocyanate. The order of elution is now established to be the order of increasing atomic number. Elution of these activities from Dowex 1 resin with $6M$ or $8M$ ammonium thiocyanate solution leaves europium and americium on the resin bed, after promethium is removed. Promethium, with most of the gamma emitters removed, may then be purified in quantities larger than 5000 curies by cation exchange.

The separation of Th(IV) and Ce(III) ions by the use of strongly acidic cation-exchange resins, such as Dowex 50 or Amberlite IR-120, has been reported recently.[7] A new method for the separation of Th(IV) and Ce(III) by using alginate as ion exchanger and dilute nitric acid as eluant is reported by Takahashi and Miyake.[16]

Alginic acid, a natural polyacid, has a property of acting as a cation exchanger for several metallic ions in a moderately acid solution of pH 1 to 3. Metallic ions adsorbed on alginic acid can be eluted easily and separately with dilute acid solutions of varying concentration. The alginate exchanger was prepared by swelling the thread of calcium alginate in a dilute sodium hydroxide solution (less than $0.1N$) for about 30 min and then by immersing in $0.5N$ nitric acid. The product was packed appropriately into a glass tube (1.5 cm in diameter, 30 cm in length) and was washed successively with 250 ml each of $0.1N$ nitric acid and distilled water. Thus the alginate was converted completely into acid form.

The mixed solution of Th(IV) and Ce(III) ions was poured onto the column, the pH being adjusted to 2 to 2.5 with aqueous ammonia. The bed was then washed with 100 ml of distilled water, and 200 ml of $0.075N$ nitric acid was passed through the column at a flow rate of about 1 ml/min. By this treatment, all the Ce(III) ions were completely eluted, and then all the Th(IV) ions remaining on the column were eluted in the same manner with 100 ml of $1N$ nitric acid. It was concluded that this method using alginate as an ion exchanger has an advantage as an industrial and analytical method for the separation of Th(IV) and Ce(III).

Miscellaneous Ion-Exchange Studies

Work is continuing at ORNL[9] on evaluation of phenolic resins for removing cationic activity from high pH fission-product wastes. More than 1000 volumes of low-level process water waste, spiked with Cs^{137} and Sr^{85} tracers and adjusted to pH 11.6, were passed through 1 volume of sodium-form Duolite C-3 resin at a flow rate of 0.7 ml/(min)(ml of resin) before the effluent activity exceeded background, corresponding to decontamination factors of about 100 for strontium and cerium. Also treated were >600 volumes at 10.6 pH and >200 volumes at 7.3 pH.

At Hanford, studies are being made to develop new types of ion-exchange equipment. In the development of the Jiggler contactor described in a previous Review,[7] efforts have been directed toward the pairing of a simple packed-bed elution with the jigged-bed adsorption column for continuous recycling of the ion-exchange resin.[17] The erratic resin flow previously experienced has been overcome by placing the elution column directly above the adsorption column (both 4 in. in diameter), introducing the eluant 6 in. above the bottom of the bed, and using a 2-ft length of $\frac{1}{2}$-in. tubing to convey the resin from the elution to the adsorption column. Several runs were made using thorium tracer feeds.[18] The most successful, operationally, was a run that lasted 11 hr.

Significant recent modifications to the Jiggler apparatus include use of an airlift to ensure that resin slurry does not clog the resin return line.[19] With a pulsing condition of $2\frac{1}{4}$-in. amplitude and 8 cycles/min, a recycling of more than 2 gal/(min)(sq ft of wet settled resin) can be maintained.

Fabrication of a 4-in.-diameter by 36-in.-long two-stage agitated-bed contactor was completed, and operational feasibility was demonstrated.[18] The stages are isolated by a resin-impervious screen, and interstage resin movement is produced by a screw pump. A resin pump of improved horizontal design was installed which improved the resin flow characteristics considerably.

A cartridge geometry has been developed at HAPO[17] for the small-diameter (3-in.) Weiss contactor.[6,7] This cartridge gives good, stable countercurrent operation. It consists of screen-

covered resin support plates spaced 5 in. apart with downcomers of $\frac{1}{2}$-in.-diameter stainless-steel tubing extending 4 in. above and 3 in. below each plate. Uniform resin flow and holdup have been obtained under a variety of flow and pulsing conditions. In general, a low-amplitude (0.08-in.) high-frequency pulse provides optimum operation. No plugging of the support screens (80-mesh) with resin particles (−20 +50 mesh) has been experienced. The results of efficiency studies[18,19] in the 3.0-in.-diameter by 48-in.-long Weiss contactor indicate good extraction efficiency and smooth, stable operation when operating as an adsorption column at feed flow rates up to 230 gal/(hr)(sq ft). Waste losses of from 2 to 7 per cent were obtained when adsorbing thorium from a feed solution containing 7M nitric acid and 2 g of thorium per liter onto Permutit SK, 20- to 50-mesh anion resin. The column temperature was 40°C.

Laboratory-scale experiments with ion-exchange resins have investigated the possible value of resins for uranium recovery from factory effluents.[20] There is now evidence that neither anion nor cation exchangers will be of value for primary stages of recovery from effluents. The conditions required for effective use of strong-base anion exchangers are being quantitatively ascertained so that these resins may possibly be used for other essential stages of recovery. A review has been made of the potentialities of ion exchange as a continuous process and of the contacting apparatus currently available.[21] The apparatus is evaluated from both technical and economic standpoints, and the design theory is outlined.

Volatility Processes

In volatility processing, uranium and plutonium are decontaminated and recovered from various types of fuel by halogenation to form volatile compounds. Progress is reviewed for various liquid-phase and dry fluorination processes as well as some processes involving chlorides.

Liquid-Phase Processing

Dissolution in NO_2-HF. Laboratory-scale work was continued at Brookhaven National Laboratory (BNL) on the nonaqueous nitrogen dioxide—hydrogen fluoride system for processing fuel elements.[22] Dissolution of Zircaloy-2

and its alloy with a few per cent uranium has been demonstrated previously.[23] Moderate dissolution rates for aluminum, aluminum-uranium alloy, and type 304 stainless steel have recently been achieved at temperatures below 200°C.

In the case of Zircaloy-2 fuel, it has been shown that the bulk of the insoluble-complex zirconium salt can be separated from the soluble-complex uranium salt by means of a series of washes and decantations. Recovery of the uranium from the decanted solution has been achieved by evaporation of the solvent and the addition of bromine trifluoride which produces uranium hexafluoride. Several flushes with bromine trifluoride were necessary to obtain high uranium recovery.

Short-term corrosion rates on Monel for a complete processing cycle involving dissolution, evaporation, drying of the salt, and opening of the system to the atmosphere have been as high as 10 mils/month at 200°C. It is believed that the corrosion rate will be considerably less in a system which is opened infrequently. Little corrosion was found during the dissolution step.

The dissolution of sintered thorium dioxide in nitrogen dioxide—hydrogen fluoride solution was not successful. It is thought, however, that unsintered material may dissolve in this chemical system.

In further work on the extraction of Pa^{233} from irradiated thorium tetrafluoride powder, a series of semicontinuous contactings with nitrogen dioxide—hydrogen fluoride solution resulted in the extraction of 32 per cent of the protactinium activity.

Fused-Salt Processing. At Argonne National Laboratory (ANL), dissolution tests of uranium-zirconium alloy fuels are being carried out in a graphite pilot-plant dissolver-hydrofluorinator, with the aim of avoiding corrosive metal-salt contact. No chemical attack of the graphite heaters was noted in about 900 hr of operation in fused zirconium fluoride—sodium fluoride salt, although one heater required replacement due to mechanical failure. A zirconium dissolution rate of 2.2 mg/(cm^2)(min) for a synthetic 10-plate fuel element was obtained.[24]

Frozen-Wall Fluorinator. One way to reduce the corrosion of a fused-salt process vessel is to operate with a layer of frozen salt on the inside metal wall. This requires the outer vessel wall to be cooled and the use of an internal heat source to keep the fluorides molten. The

technical feasibility of providing internal heat by induction heating or by electrolytic heating has been shown earlier. Further development work on the pilot-plant scale was done at ANL on the electrolytic heating method.[24]

The salt used in these tests was approximately equimolar sodium fluoride–zirconium fluoride. The container was a Monel vessel 17 in. in diameter and 52 in. high with a dished bottom.[7] Water cooling coils were bonded to the outside of the vessel in five zones from bottom to top. The electrodes were made of 2-in. nickel pipe. Electric power was brought in to the bottom of the electrode through a $3/4$-in.-diameter copper rod. Introduction of power at the bottom of the electrode rather than at the top was done to prevent "shorting out" of power at the surface of the salt, which had previously resulted in poor heating at the bottom. The vertical electrodes, about 7 in. apart, were supported at the top and were positioned $1\frac{1}{2}$ in. from the bottom. Average resistance between electrodes was 0.025 ohm for a 26-in. salt depth and 0.019 ohm for a 36-in. salt depth. Separate electrical resistance heaters in the annuli of the electrodes were used initially to melt a salt path between the electrodes; thereafter all heating was done electrolytically by current passage through the molten salt. Alternating current between 16 and 25 volts was used in the tests.

The thickness of the frozen wall was maintained quite uniformly in the range of $\frac{1}{2}$ to 1 in. on the wall and 1 to $1\frac{1}{2}$ in. on the bottom with a power level of approximately 1.5 kw per square foot of frozen wall. Power density in the molten salt appeared to be the controlling variable with respect to wall thickness.

Other than by direct observation, the presence of the frozen wall was indicated by a high electrical resistance between the electrodes and the vessel wall. Measured values of over-all wall resistance varied from 1600 to 78,000 ohms, as obtained with a 30-volt d-c bridge circuit with the positive side connected to the vessel wall. These measurements can be used to control electrode power input for salt heating.

Two problems are encountered in this system: (1) corrosion of the electrodes and (2) formation of salt crust at the interface. The electrode corrosion amounted to dimensional attack of 10 mils/day and was concentrated at the point of maximum current density. (No fluorinating agent was involved in these tests.) Thus fairly fre-

quent electrode replacement would be required. The formation of solid salt crust at the top was progressive with time and resulted from high heat losses at the top of the vessel. External heating would be required to melt back this crust at the top, although it was found that the frozen wall at the sides could be melted back by electrolytic power alone.

Dry Halogenation and Fluidization Process

Direct gas-phase halogenation of fuels has always seemed to be desirably simple, but control of the high heat of reaction has presented problems. The use of fluidized beds to provide good heat transfer offers a technique for carrying out direct gas-phase halogenation of metal and other solids in a controlled manner. For cases in which the solid is not directly fluidizable, the charge may be immersed in a fluid bed of inert particles. This method is being applied to various volatility processes.

Zircex Process. The Zircex process involves hydrochlorination and volatilization of zirconium from zirconium-matrix or clad fuels, followed by aqueous dissolution of the uranium residue. In a modified process, chlorination and sublimation of the uranium-bearing residues with carbon tetrachloride gave lower uranium losses.[2,25,26]

Fluid-Bed Hydrochlorination of Zirconium-Matrix Fuel Elements. At BNL a number of preliminary pilot-plant-scale experiments have been performed on the hydrochlorination of typical zirconium alloy fuel elements in a fluid-bed reactor.[22] The reactor vessel consisted of a 6-in.-diameter hydrochlorination chamber, 32 in. long, which enlarged to an 8-in.-diameter disengagement section, 20 in. long. A porous metal plate was located between flanges at the lower end of the hydrochlorination section and served to support the inert fluidized bed (probably sand) as well as to distribute the fluidizing gas. The top of the vessel was closed by a flange which contained a 5-in. gate valve, used as a charging port for the fuel elements. Thermocouple probes and pressure taps also entered through the top flange.

During operation the heat of reaction was removed by means of a blower which forced cooling air to flow past the outside of the hydrochlorination chamber. This section was provided with copper fins to facilitate heat transfer, as well as Calrod heaters to bring the vessel up to

operating temperature, and was surrounded by a sheet-metal shroud, thereby forming an annular flow channel for the cooling air. Effluent gases from the process entered the 1-in. off-gas line through a metal edge filter which was located inside the disengagement section of the vessel.

conium dioxide coating. The results of these experiments are listed in Table IV-4. In Runs 6, 7, and 8, two thermocouples were inserted between the two middle plates of the fuel-element section. One thermocouple was positioned approximately 1 in. above the upstream (lower)

Table IV-4   FLUID-BED HYDROCHLORINATION OF ZIRCONIUM-MATRIX FUEL ELEMENTS[22]

Run No.	Element type	Weight, g	Av. surface area, cm²	Elapsed run time, min	Bed temp., °C	Approx. vol.% HCl	Max. plate temp. 1 in. from upstream end	Max. plate temp. 6 in. from upstream end	Approx. % HCl conversion	Weight loss, %
1	Single-plate	425	635	5	400 − 425	50				10
2	Single-plate	382	627	10	450 − 475	80				42
3	26-plate	4,947	10,400	30	375 − 450	82			35	28
4	26-plate (remainder from Run 3)	4,995	6,600	55	430 − 490	83			26	77
5	7-plate autoclaved	2,070	2,265	20	450 − 480	84			9	22
6*	26-plate	7,025	11,000	7	370 − 425		885	710		9
7	7-plate (remainder from Run 5)	1,620	1,927	35	440 − 470	80	610	565	6	44
8	26-plate	6,390		15	425 − 490	81	740	650	25	23

*Shut down due to high filter pressure drop.

This section also joined to a 3-in. pipe which contained a rupture disk for overpressure protection. Fluidizing and reactant gases were metered from a manifold at the control panel into the bottom of the reactor. The off-gas line led to an open 100-gal glass-lined tank fitted with a glass-pipe dip tube. The tank contained 80 gal of water which served to absorb the volatile zirconium tetrachloride product and excess hydrogen chloride. This absorber tank was located outside the building, and unabsorbed effluent gases, chiefly hydrogen and nitrogen, were released to the atmosphere and dispersed. There was no provision for recovering zirconium tetrachloride; however, it is planned to install an experimental fluidized-bed desublimer in the near future.

Two runs were made using a single fuel plate, 15 in. long, to check out the operation of the unit. All subsequent experiments have been made with 10-in. lengths of multiplate fuel-element subassemblies. These subassemblies were of two types: a 26-plate section with 45-mil spacing between plates, and a seven-plate section with a spacing of approximately 80 mils between plates. The seven-plate subassembly was autoclaved and had the characteristic zir-

end, and the other, 6 in. above the upstream end. The high metal temperature attained in the case of the 26-plate sections is to be expected in view of the high over-all rate of reaction and the small spacing between plates. The middle plates of these sections appear to be somewhat more aggressively attacked than the end plates, probably due to the higher temperature in this area. It is planned to carry out experiments with beds of smaller particle size which may facilitate heat transfer from the inner plates. Comparison of the results of Run 5 with those of Run 7 indicate that the oxide coating did not significantly interfere with the progress of the reaction.

It is significant to note that the temperature of the fluidized bed was most responsive to control during hydrochlorination, even though large amounts of heat were released. Even under adverse conditions there was no danger of an uncontrolled reaction. For example, in Run 6 the pressure drop through the filter increased to the extent that gas flow was insufficient to maintain fluidization of the bed, at which time the bed temperature began to rise sharply. The hydrogen chloride was shut off, and the bed was again fluidized with a higher flow of nitrogen. The reaction ceased immediately, and rapid bed cooling followed.

Fluorination Processes. Other schemes involving the volatility of uranium hexafluoride for processing irradiated fuels are under study at ANL. These include a direct fluorination process and the aqueous dissolution dry fluorination (ADF) process.[24]

The direct fluorination process now under study involves direct fluorination of oxide matrix with fluorine or other fluorination agents to produce volatile uranium hexafluoride and plutonium hexafluoride. Allied reactions of intermediate compounds are being studied. Equilibrium constants for the reaction $PuF_4 + F_2 \rightleftharpoons PuF_6$ have been determined in the temperature range 150 to 400°C. The results may be represented by the equation

$$\log K = \frac{-1331}{T} - 0.275$$

The use of sulfur tetrafluoride as a fluorinating agent is being investigated in reactions with certain uranium and plutonium compounds. In thermobalance tests, reaction with sulfur tetrafluoride was found to occur readily with uranium trioxide and uranyl fluoride above 300°C. Reaction with uranium dioxide and U_3O_8 was incomplete. No reaction was found with uranium tetrafluoride, plutonium dioxide, and plutonium tetrafluoride.

Consideration is being given to fluoride volatility processing of uranium dioxide fuels. Work is under way at ANL on the pilot-plant-scale investigation of direct fluorination of dense uranium dioxide pellets.[24] Because the uranium dioxide pellets most frequently used as nuclear fuel are too large to be fluidized directly, the use of an inert fluidized medium such as magnesium fluoride to fill the void spaces in a packed bed of pellets has been considered. The inert bed would aid in the removal of heat and in the retention and dilution of reagent fines and radioactive residues. Observation of such fluidized systems was made in glass mockup equipment.

Preliminary runs in a 3-in.-diameter fluid-bed reactor were made using 10 per cent fluorine in nitrogen at 400 and 500°C. Very substantial quantities of fines were produced by chemical pulverization of the uranium dioxide, but at 500°C the amount of fines was small.

Additional work was performed on the ADF process being developed for the recovery of uranium from low uranium–Zircaloy-2 fuel alloys. The process involves aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry powder, and fluorination of the powder to remove and recover the uranium as the volatile uranium hexafluoride. Studies of the drying step have included use of high-zirconium feed solution (3.6M zirconium) and dilute zirconium feed solution (1.5M zirconium) at feed rates up to 150 ml/min and 210 ml/min for concentrated and dilute feed, respectively. An internal auto-resistance type Inconel strip heater has been introduced into the fluid bed to provide additional capacity to the dryer.

Investigation of the fluorination step included study of the hydrofluorination of dryer product at 300°C with equal mixtures of hydrogen fluoride and nitrogen to provide feed materials with low residual water and oxygen content. Static-bed fluorination studies on the uranium-zirconium fluoride dryer products have been carried out in bench- and pilot-scale fluorination reactors. Uranium removals greater than 99 per cent have been achieved in 1- to 3-hr runs at 700°C.

Kinetics of Reaction of Bromine Trifluoride and Fluorine

Bromine forms a series of compounds with fluorine of varying degrees of fluorination potential. Bromine trifluoride and bromine pentafluoride have been studied extensively as liquid and vapor fluorinating agents in volatility processes. The kinetics of the gas-phase reaction of bromine trifluoride and fluorine to form bromine pentafluoride have been studied from 68 to 121°C in a nickel reactor and with the initial pressures varying from 30 to 300 mm. The reaction is bimolecular, homogeneous, and has an activation energy of 16.4 kcal. The observed frequency factor of 2.6×10^{11} cc/(mole) (sec) corresponds to a probability factor of 10^{-3}, thus indicating that only a part of the bimolecular collisions of sufficient energy to cause reaction actually results in the formation of bromine pentafluoride.[27]

Pyrometallurgical Processing

Pyrometallurgical processes are those in which the metallic state of the fuel is retained during processing or is readily produced as an intrinsic characteristic of the process. An ex-

ample of the latter is molten salt electrolysis in which the metallic character of the fuel is lost momentarily in passage through the salt bath. These processes are in a relatively early stage of development; they are generally not high-decontamination processes and aim to provide control of fission-product and fissionable-material concentrations on the basis of reactor requirements. Consequently, remote fabrication is an integral feature of such processes.

The potential economic advantages result mainly from ability to process short-cooled fuels, from the avoidance of chemical conversion, and from process simplicity. Offsetting these is the necessity of remote operation throughout the entire fuel cycle. The actual economic situation cannot yet be given, requiring both further process development and large-scale demonstrations to provide economic data.

Processes having these same characteristics are being sought for ceramic fuels. Although they cannot be called pyrometallurgical processes, they are pyrochemical and, on the basis of similarity of goals, are included in this section.

Melt Refining

To enable undelayed and contiguous recycle of fuel, a processing plant incorporating pyrometallurgical processing methods is being built adjacent to the Experimental Breeder Reactor No. II (EBR-II) at the National Reactor Testing Station in Idaho. The initial processing procedure for discharged fuel will be melt refining, simple melting of the fuel under conditions which provide for removal of many fission products by selective oxidation and volatilization. Processes are also under development for incorporation into this plant which are based on the use of liquid-metal systems as solvent and processing media for the uranium and plutonium fuels of interest.

Since the melt-refining process does not provide high decontamination from fission products, all operations, including refabrication, must be carried out by remote operations. Status of the design and construction of the processing plant and the development of equipment components is given in ANL Chemical Engineering Division quarterly reports, the latest being that for the first quarter of 1960 (reference 28). Viewing is provided by thirty-two 5-ft-thick special glass windows and by high light intensity within the

cell to overcome light attenuation in the thick windows. An inner removable slab of glass contains 2.4 per cent ceric oxide to make it resistant to darkening by radiation. Casting of the glass is nearly complete, and assembly of the window units has been started.

Equipment operation and movement of materials within the cell are effected by heavy-duty cranes and manipulators. The cranes are under construction. Bids will soon be placed for fabrication of the manipulators, models of which have been under test at ANL.

Selection of materials which will withstand the high radiation intensity within the cell and large accumulated radiation dosages (over 10^{10} rads) is an important matter. The effect of radiation is being determined for all materials considered for use in the cell. Although most materials are metal or ceramic and show good stability under radiation, radiation-resistant greases are very desirable in connection with manipulator and crane operation. A grease designated California Research 159 has shown usability to 3×10^9 rads.[28] This dosage is equivalent to about six years' exposure in the cell.

Equipment designs for the Idaho facility are being tested in a mockup facility at ANL. The melt-refining furnace is being employed for preparation of the entire first core loading using remote operation procedures. Fifty-eight of the necessary eighty 10-kg ingots of enriched fuel have been prepared to date.[28] Some deficiencies of the zirconia crucibles employed have been exposed by these runs and are being investigated jointly by the manufacturer and ANL. Considerable refinement of operating techniques and many improvements in equipment have resulted from these runs. These include an improved fume trap for capture of the volatiles, better insulating material, and better mold designs.

A terminal report[29] has been issued for the Processing Refabrication Experiment (PRE), an engineering experiment to demonstrate the remote processing and refabrication of power-reactor fuels. The process was initially based on processing metallic fuels by a melt-refining type process, but the program was later reoriented to processing and reconstituting uranium oxide fuels. Cell designs and the process, handling, and maintenance equipment are well described. It was concluded that such facilities can make significant contributions to low-

decontamination process concepts, and it was recommended that this type of experiment be conducted for other processes which are now under way.

Liquid Metal and Salt Processes

The chemistry of various liquid-metal systems is being studied, in connection with the development of liquid-metal processes, to provide the appropriate basic data for process design. This is a continuing program to develop the necessary solubility and thermodynamic data for systems of interest. Additional solubility and thermodynamic data for various elements in zinc and cadmium have been reported.[28]

Cadmium solutions of uranium have been found to be very sensitive to impurities which cause precipitation of the uranium.[28] Substances which effect such precipitation are iron, nickel, silicon, aluminum, graphite, and boron nitride, most of which are constituents of candidate container materials. This behavior contrasts with the stability of uranium-zinc solutions and results from high activity coefficients of uranium in cadmium solutions.

Work was continued at ANL on a process for recovery of the fissionable material remaining as a "skull" in the zirconia crucible after a melt-refining operation.[28] The process must also accomplish some purification of the fissionable material. Oxidation by an oxygen-argon mixture smoothly converts the skull to a powdered oxide in 5 to 6 hr at 700°C. The powdered oxide may be easily removed from the crucible by pouring. The skull oxides are reduced in magnesium alone or dissolved in a liquid-metal solvent such as zinc or cadmium. A fused chloride salt is often used to promote reaction of the uranium oxide powder with the liquid metal and also to serve as vehicle for removal of the magnesium oxide formed in the reaction. A drawback to the use of the fused salt is the accelerated attack on construction materials.

High oxide-reduction yields (90 to 95 per cent) have been achieved in pure magnesium at 850°C and in various magnesium-zinc-cadmium systems[28] at 800°C. Reduction times have ranged from 6 to 13 hr using mechanical agitation. Ultrasonic agitation is also being investigated to effect suspension of oxide particles and also to promote uranium dissolution in molten-metal systems.[30] Separation and purification of ura-

nium from the resulting metal solution will be effected by fractional crystallization steps and distillation of the solvent metals.

Although the reduction of uranium oxides is an important step in the above process, a more important application of such reduction may be made in the processing of oxide or carbide fuels. Uranium carbide may be easily converted to the oxide for processing purposes.[31]

One of the methods by which plutonium can be separated from uranium in a liquid-metal system is by utilizing the high solubility of plutonium and the low solubility of uranium in magnesium. A magnesium or magnesium-rich solution can easily be produced by appropriate process design. After separation of the magnesium phase, the plutonium is recovered by vaporizing the magnesium. The recovery of plutonium from a magnesium solution has been demonstrated on a 100-g scale in tantalum equipment.[32] Essentially complete recovery of the plutonium was realized, less than 0.1 per cent being entrained in the magnesium vapor. The recovered plutonium product was in the form of a very clean button.

A similar process is currently being employed to effect the separation of uranium from thorium blanket material at Atomics International and is based on the high solubility of thorium and the contrasting low solubility of uranium in molten magnesium. The process consists of separation of insoluble uranium followed by a subsequent recovery of the thorium from the thorium-magnesium solution by hydriding the thorium and filtering it. Thorium hydride has been successfully recovered from liquid magnesium by filtration.[31] The thorium concentrates have been dehydrided, and the magnesium has been partially removed by heating to 750 to 800°C under vacuum. Process demonstration experiments have been made which indicate reasonably good (around 90 per cent) recovery of the uranium in a magnesium concentrate.

The use of distillation as a major unit operation in liquid-metal processes has prompted the construction of large-scale metal distillation units at ANL.[28] One such unit having a distillation capacity of 100 kg of cadmium per hour is under construction. Another with a distillation capacity of 10 kg/hr is now in operation on a 50-kg (cadmium) scale (see Fig. 5). DeVoe has recently discussed the application of vacuum
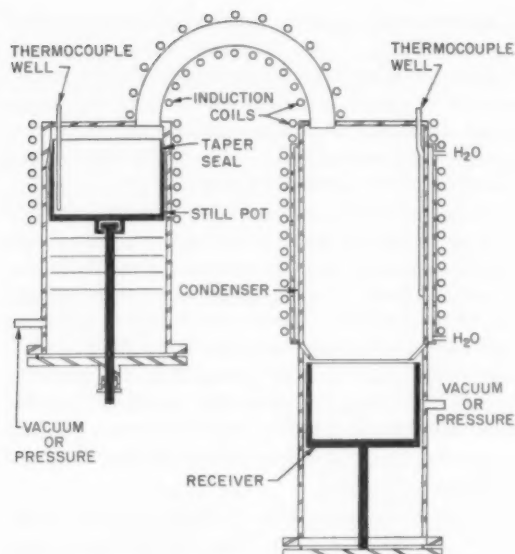
Figure 5 — Cadmium distillation unit.[28]

distillation of metals to radiochemical separations.[33]

The use of aluminum as a solvent medium in which to process metallic fuels is being explored by the Dow Chemical Co. The solubility of uranium in aluminum was determined over the temperature range 670 to 850°C and is given by the equation[34]

$$\log (\text{wt.\% uranium in solution}) = 2.530 - \frac{1286}{T}$$

Solubilities of uranium and various fission products in aluminum alloys were also reported.[35] A subcontract was arranged with the Battelle Memorial Institute (BMI) to investigate the behavior of plutonium in the Dow process.

An investigation is under way to determine the applicability of the Dow process to separation of uranium from zirconium in zirconium-aluminum alloys.[34] Such alloys are corroded by molten uranium, the zirconium precipitates as $ZrAl_3$, and the uranium is dissolved. Little co-precipitation of the uranium with the $ZrAl_3$ occurs.

Mercury is another liquid-metal solvent for uranium, thorium, and plutonium. The thermodynamic properties of the uranium mercurides have recently been reported.[36]

The ARCO* process under development by Phillips Petroleum Co. is a fused-salt pretreatment step which provides separation of zirconium from uranium. It consists of reaction of the fuel with excess molten lead chloride to produce zirconium tetrachloride which volatilizes, and uranium tetrachloride and uranium trichloride which both dissolve in the lead chloride. The lead chloride — uranium chloride phase diagram is currently being developed.[37] The separated salt phase can be dissolved for aqueous processing or further processing pyrochemically. Satisfactory removal of uranium from the fused-salt matrix has been effected by refluxing with nitric acid.

Corrosion testing[37] of various materials is under way in a molten lead — lead chloride system at 528°C. Incoloy 804 and Inconel X have shown reasonably good resistance with corrosion rates of 0.3 and 3 mils/month, respectively. Hastelloy F and Carpenter 20 stainless steel, Haynes Alloy C, Croloy-2¼, tantalum, and molybdenum were more severely attacked, corrosion rates ranging from 5 to 81 mils/month.

Thorium Fuels. Two methods are currently being investigated for processing thorium fuels: molten salt electrorefining and aluminum reduction of thoria in cryolite. In the electrorefining process, it was expected that the impure thorium would be dissolved anodically into the fused-salt bath (NaCl-KCl) and deposited in a molten zinc cathode. However, although thorium dissolved, it later precipitated in the salt bath rather than transferring to the molten zinc electrode.[38] A topical report has been issued on the electrorefining of irradiated thorium-uranium alloys.[39] The material was previously reported in an earlier Review.[25]

In the thoria reduction process, thorium oxide is mixed with molten cryolite and reduced with metallic aluminum at 1050°C to produce a thorium-aluminum alloy. High reduction values of over 90 per cent have been encouraging.[31],[38] A set of reduction experiments was carried out at 1050°C to determine the effect of cryolite-thoria ratio on reduction yields.[38] The highest yields were obtained at a cryolite-thoria ratio of about 4. The effect of thorium concentration in the aluminum phase on the reduction yield was also studied. The reduction yields were 97, 78, 44, and 0 per cent, which resulted in con-

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*See also page 8 of this Review.

centrations of 19, 32, 39, and 39 wt.% thorium, respectively, in the aluminum ingot, indicating that about 40 wt.% is the maximum concentration of thorium in aluminum which can be prepared by this method. The presence of aluminum oxide in the salt phase was also found to inhibit the reduction.

Preparation of High-Purity Yttrium. A 20-lb batch of high-purity yttrium metal was prepared by the metallothermic reduction of yttrium trifluoride with a mixture of calcium and magnesium in a tantalum crucible.[40] The resulting metal was contacted with a fused yttrium chloride—calcium chloride mixture and then with yttrium chloride to extract oxygen and other impurities. Tantalum pickup was negligible. Other impurities were 435 ppm oxygen, 60 ppm carbon, 6 ppm nitrogen, and 70 ppm fluorine. A poor reduction yield (only 20 per cent) was realized using a calcium chloride—lithium chloride salt mixture in contact with a zinc-calcium alloy at 900°C. An electrolytic approach was also tried, but no yttrium metal was obtained.

Processing of Ceramic Fuels

Work is in progress at several sites on the development of simple recovery and refabrication processes for highly irradiated, short-cooled uranium oxide and other ceramic fuels. The "salt-cycle process" under development at Hanford involves dissolution of uranium oxide in a eutectic of sodium and potassium chlorides by the action of chlorine to produce UO_2Cl_2. This is followed by electrolytic reduction to recover the uranium oxide. Appreciable fission-product removal is realized by retention of fission products in the salt phase. Good fission-product removals have been realized for rare earths, strontium, cerium, barium, and zirconium-niobium.

It is desirable that the uranium dioxide crystals (which are of near theoretical density) deposit in a porous and dendritic manner to enable easy removal. Although this type of deposit was realized in small-scale experiments, in larger-scale studies much less manageable uranium dioxide products have been formed.[18,19,41] Instead of concentrated crystalline powders amenable to compaction by swaging, the larger-scale work has produced deposits which are difficultly removed from the graphite cathode and then only as hard flakes. It has been found that the degree

of exposure to chlorine markedly influences the crystal habit of the uranium oxide produced electrolytically. The deposit is dendritic if exposure to chlorine is limited and hard and dense if not limited. Alternate cathode materials are also being investigated in view of the high carbon contents of the product (as high as 1500 ppm).

Uranium dioxide formed by electrolytic reduction of uranyl chloride in the presence of excess uranium dioxide was found to deposit as platelet crystals from a potassium chloride—sodium chloride eutectic. The crystal habit of the uranium dioxide initially present as dendritic crystals was also largely changed to the platelet form. This suggests that the tendency for the uranium dioxide to crystallize preferably as platelets is thwarted by the conditions of electrolytic deposition.

A variable behavior of plutonium has been found in this process. The possibility that co-deposition of plutonium and uranium can be controlled and utilized to generate a single blended product for recycle is an intriguing one and has prompted further studies of plutonium behavior in the salt-cycle system.

Alumina and high-density carbon are considered good possibilities as construction materials, neither being affected after 10 days' exposure at 800°C to the potassium chloride—lithium chloride salt mixture.

A method of cyclic oxidation and reduction by gaseous reactants is being investigated at Atomics International[2] for low-decontamination processing of uranium dioxide fuels. Although some decontamination from cesium, ruthenium, tellurium, iodine, and the noble gases is achieved by this process, the primary goal is re-enrichment and refabrication of the fuel shapes.

Work is now under way to demonstrate technical feasibility of the oxidation-reduction process for high-burnup uranium dioxide fuels which have been irradiated to several thousand megawatt-days per ton of fuel.[31] The apparatus has been fitted into the process cell, and some of the equipment has been checked out. Larger-scale engineering equipment is also being developed for reprocessing and refabrication of uranium dioxide fuels. These are inactive experiments in which kilogram quantities of simulated high-burnup uranium dioxide will be processed. The effect on fabrication of fission-product buildup, as represented by the addition of stable isotopes to the uranium dioxide, is also being investigated.

Uranium Oxide Fuels. Chlorination of uranium dioxide pellets by carbon tetrachloride at 800°C has also been studied with the following results:[36]

1. Uranium dioxide pellets volatilized readily and completely.

2. Sintered thorium dioxide reacted very slowly, small additions of uranium dioxide causing the reaction to become more rapid.

3. Oxides of the rare earths formed only nonvolatile chlorides. Zirconium oxide was volatilized.

4. Of the various construction materials, only silica, Vycor, and graphite appeared satisfactory; stainless steel, nickel, tantalum, tungsten, and silver were rapidly destroyed, and alumina was attacked.

Uranium Carbide Fuels. Two alternate methods are being considered for the pyrochemical processing of uranium carbide fuels. In one method, the carbide is reacted with oxygen to yield uranium oxide which is subsequently reconverted to the carbide by reaction with the carbon at elevated temperatures. In the other method, the carbide (or oxide produced in the above process) is chlorinated, and the uranium chloride is volatilized to separate some fission products and is then reconverted to uranium carbide.

Oxidation of uranium carbide begins[38] at the region 225 to 240°C. Chlorination experiments of uranium dioxide pellets containing 1 and 5 per cent fissium with carbon tetrachloride at 800°C resulted in a recovery of uranium as the chloride of 97 to 99 per cent. A direct treatment of uranium carbide with hydrogen chloride gas gave a rapid reaction at 500°C and rapid evaporation of uranium at 750°C, apparently as uranium tetrachloride.

Homogeneous Reactor Processing

The homogeneous reactor concept has the potential advantage that a sidestream of the fuel can be removed either continuously or on a frequent batch basis for chemical processing. The aqueous Homogeneous Reactor Test (HRT) at Oak Ridge is one such reactor utilizing this concept. The performance and development of a chemical processing plant associated with the reactor are reported here.

The primary processing method is the separation of solids consisting of corrosion and fission products from a sidestream of fuel by means of

hydroclones. To increase the capacity of the hydroclone system, an assembly of a number of hydroclones in parallel was installed in the plant ahead of the final collecting hydroclone. An increase in solids removal rate by a factor of 3 was predicted. Initial removal rates were high, about 5 g/hr, but these gradually decreased over a period of 500 hr to a removal rate of $\frac{1}{2}$ g/hr. This is 50 to 80 per cent higher than previously obtained. It is suspected that the circulating solids have particle sizes which are smaller than estimated and hence are affecting hydroclone efficiency. The chemical compositions of the corrosion products collected have been similar to those previously obtained.[42]

A new method has been proposed for processing the fuel from the HRT.[42] The fuel is brought into contact with hydrogen. This precipitates the uranium as uranium dioxide and copper as metallic copper, leaving in solution the nickel, cesium, and perhaps other fission products. In preliminary experiments a solution consisting of 9.9 g of uranium per liter, 0.60 g of copper per liter, and 0.735 g of nickel per liter in $0.034M$ D_2SO_4 (in D_2O) was used; 50 ppm iodine, 20 ppm cesium, and 100 ppm neodymium were also added. This mixture was heated at 250°C under a 100-psi atmosphere of deuterium. Within 7 hr, uranium and copper concentrations had decreased to 0.05 and 0.04 g/liter, respectively. In an additional 15 hr, corresponding concentrations were 0.024 and 0.04 g/liter. The nickel and cesium remained in the solution; the neodymium concentration decreased from 100 to 60 ppm, and the iodine, from 50 to 6 ppm. After 22 hr the solution was drained, leaving the precipitate behind. Uranium and copper were then reconstituted in $0.07M$ D_2SO_4 under an oxygen atmosphere of 200 psi. Within 2 hr at 250°C the original solution was essentially restored minus fission products. Uranium and copper recoveries were above 99 per cent.

A topical report on hydroclones has been published.[43] Engineering correlations based on experimental studies are presented on the batch accumulation of solids separated from solid-liquid feeds.

Plant Design, Instrumentation, and Equipment Development

A 1954 report recently declassified[44] estimates the cost of a directly maintained solvent-

extraction plant to process 3 metric tons of uranium per day. The fuel is assumed (1) to be irradiated to give 550 g of plutonium per metric ton of uranium, (2) to be cooled 120 days, and (3) to have as products a concentrated aqueous uranyl nitrate solution and a concentrated aqueous plutonium nitrate solution. The plant is estimated to have a fixed investment cost of $32,170,000 and an annual operating cost of $3,320,000.

An investigation of design and scaleup of mixer-settlers as a part of the Dapex solvent-extraction process for recovery of uranium from sulfuric acid leaching of ores has been reported.[45] The basis for design of equipment for the process was obtained by a unit operation study of the variables affecting rate of extraction in the mixer and of phase separation in the settler. Scaleup relations were developed from data obtained in three sizes of geometrically similar units. This information, together with chemical flow-sheet demonstration in laboratory-size multistage equipment, was used as a basis for design of full-scale plants without operation of a pilot plant. The study concluded:

1. The rate of uranium extraction in the Dapex process is proportional to the cube root of power input for both batch and continuous flow if the extraction in the mixer only is measured.

2. Mixers can be scaled up by geometric similitude at constant power input per unit mixer volume, demonstrated in 6-, 12-, 20-, and 36-in.-diameter mixers, representing a volumetric scaleup ratio of 200 to 1.

3. The flow capacity of settlers is characterized by a band of dispersion at the interface, the thickness of which is a measure of the approach to flooding.

4. Settlers can be scaled up based on flow rate per unit cross-sectional area, demonstrated in settlers 6 in. to 16 ft in diameter, representing an area scaleup ratio of 1000 to 1.

5. Control of mixing to form water-in-oil dispersions is recommended to minimize solvent entrainment and the formation of emulsions with solutions containing colloidal materials which stabilize oil-in-water emulsions.

A theoretical analysis of pulse columns[46] was made using a stagewise approach to the problem. The column was assumed to be divided into discrete stages, each stage having been defined as that part of the column between two adjacent perforated plates. The cyclic reversal of flow which is characteristic of the pulse column permitted more material-balance equations to be written than for a simple countercurrent extractor.

The operation of the pulse column was described mathematically using material-balance equations and, from the theory developed, a design method was derived which used two "stage" lines and two "operating" lines, one set for the upstroke and one set for the downstroke of the pulse generator. The stages could be stepped off between each of these sets of lines in much the same manner as is done on a McCabe-Thiele diagram. Assuming equilibrium contact, the effect of recycle in a pulse column was shown to cause a large decrease in the separation obtained as the pulse frequency was increased. To account for nonequilibrium contact, two stage efficiencies were defined: one for the upstroke and one for the downstroke half cycle.

Holdup studies were made using two systems, isoamyl alcohol—water and methyl isobutyl ketone—water. Under proper operating conditions the holdup, per cycle, of the dispersed phase for both systems was shown to be equal to the interstage flow, per cycle, of the dispersed phase. Also for both systems the stagewise holdup per cycle first decreased and then increased as the pulse frequency was increased. With the water phase discontinuous, a sharp increase in the dispersed-phase holdup was observed at critical pulse frequencies for the isoamyl alcohol—water system. The critical frequency was a function of the superficial flow rate of the dispersed phase. This break in the holdup curve was attributed to a hindered settling effect due primarily to the high viscosity of the continuous isoamyl alcohol phase. Holdup behavior at high frequencies was quite different for the two systems.

Extraction runs were made using the system methyl isobutyl ketone—acetic acid—water. It was shown both theoretically and experimentally that, even though the stage efficiencies may increase, the over-all separation performed by the column may decrease with increased pulse frequency because of the effect of recycle. The stage efficiencies were lower for that half cycle in which the wetting fluid passed through the plates. The over-all operating line shifted closer to the equilibrium line as the pulse frequency was increased, theoretically due to the unequal effect of recycle on the end sections of the

column as compared with the recycle effect in the stages.

On the basis of the theory presented for a pulse column operating in the emulsion region, it was found to be theoretically possible for a column to be operating in a pinched-in region, even though this is not apparent by an examination of the superficial flow rate ratio of the two streams being fed to the column. The change in the phase composition would change the actual interstage flow ratio between the stages and thus alter the slopes of the over-all stage line and the over-all operating line.

Sampling techniques were developed to take samples of the interstage flow streams in a column operating in the mixer-settler region. Samples were taken by forcing hypodermic needles through rubber stoppers in the column and then inserting the tips of the needles through holes in the plates. Removal of the sample from the column during the desired part of the pulse cycle was controlled by microswitches located on the pulse generator. The microswitches operated specially constructed solenoid valves in the sampling lines.

In many liquid-extraction systems, measurement and control of the interface between the organic and the aqueous phases is a continual maintenance problem when using conventional level-sensing devices such as pneumatic or hydraulic differential pressure units. The problem is especially acute when the solutions contain dissolved salts which tend to crystallize and cake up the impulse lines, or when corrosive attack on the differential pressure cell occurs. The use of inert sealant fluids in the impulse lines offers only a partial solution to the problem.

The use of a bridge circuit containing balanced thermistor sensing units has become attractive in the past few years with the development of reliable, age-stable thermistors. Use of these devices for determining liquid level has been proposed by Soble[47] for situations where the interface to be detected is liquid against air. This idea can be expanded to detect liquid-liquid interfaces[48] by placing a number of thermistors in series as a sensing element over the desired range of liquid interface control as shown in Fig. 6.

A thermistor is a ceramic material which has a negative coefficient of resistance, i.e., decreasing electrical resistance with increase in temperature. This change in resistivity with

temperature is so high in some materials that the resistance can be doubled with a temperature change as little as $15°C$. Thermistors can be secured with a glass coating which permits direct exposure to most process fluids.
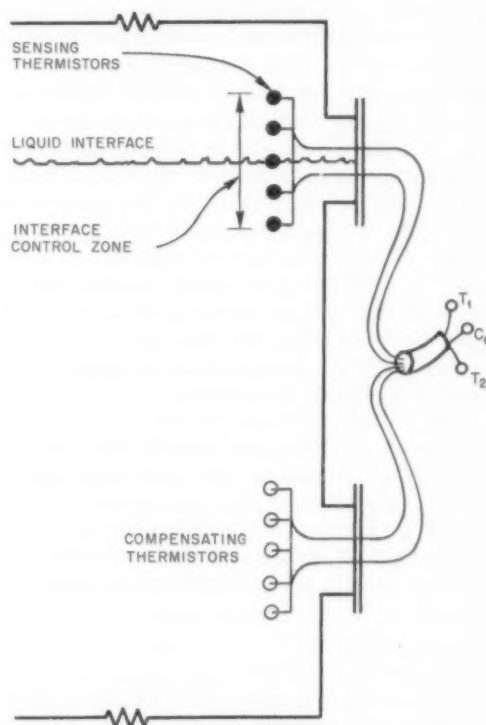

Figure 6 — Interface sensing-element location.[47]

In operation, the thermistors are heated slightly above the temperature of the ambient fluid by the passage of a small current. The current that can pass is governed by the rate of heat conduction away from the thermistors, and the rate of heat loss is a function of both the thermal conductivity and the specific heat of the surrounding liquid. Since the thermal conductivity of water is about three to four times that of most organic materials, while its specific heat is twice that of organics, a change in the environment surrounding the thermistor from water to organic will cause a measurable increase in thermistor temperature, with an accompanying change in the resistivity of the circuit which can be measured on a Wheatstone bridge.

A protected alpha-sensitive scintillation screen has been developed[49] which can be used in direct contact with aqueous or organic liquid process streams, yielding a measure of the concentrations of alpha-emitting radioisotopes in the stream. Concentrations of 0.05 to 10 g of plutonium per liter can be measured with a precision of about ±20 per cent; and the detection level is about 0.01 g/liter. Because of the lesser sensitivity of screen to beta and gamma emissions, relatively high fission-product levels can be tolerated without serious interference. In a sample cell having a low volume to active area ratio, 10 curies of Cs^{137} per liter is equivalent to only 0.01 g of plutonium per liter.

The scintillation screen consists of a thin layer of activated zinc sulfide sandwiched between a transparent backing plate and a thin ($\frac{1}{4}$-mil) Teflon film. The film is firmly bonded, by fusion, to the surface of the backing plate — a lower melting fluorocarbon.

Sample cell assemblies have been designed and tested, and prototype instruments have been installed and evaluated. The instrument appears to be very satisfactory in clean streams of less than $2.5M$ nitric acid but probably is not suited to streams of higher acid concentration or to those containing abrasive particulate matter.

Corrosion

The selection of adequate construction materials is an inevitable part of all chemical process developments. Modifications of existing processing procedures for reactor fuels also necessitate a critical appraisal of materials. As many of the developments in the chemical processing of nuclear fuels involve more than usually corrosive chemicals, it has been desirable to set up separate corrosion programs to arrive at sound selections. It is the intent in this section to cover recent developments in these programs.

Solvent Extraction

Nuclear fuels are at present processed by solvent-extraction techniques at four AEC sites. Existing plant procedures are not capable of handling some of the newer fuels. So-called head-end treatments have been developed to adapt these plants to these fuels. These vary according to whether the cladding of the fuel is zirconium or zirconium alloy, stainless steel, or aluminum. A desirable objective is to find a construction material that is compatible with processes handling all three types of cladding.

In general, fuels having an enrichment of less than 5 per cent will be processed at Hanford. The cladding of zirconium fuels will be removed by the Zirflex process (ammonium fluoride), and the cladding of stainless-steel fuels will be removed by the Sulfex process (sulfuric acid). Hanford has found that vacuum-melted Hastelloy F is sufficiently compatible to both procedures to be used as a construction material for a single head-end treatment dissolution vessel. For pilot-plant studies of the Darex process for stainless-steel fuels (nitric acid—hydrochloric acid), Hanford has a titanium dissolver and associated equipment.

One of the limitations of commercial Hastelloy F is its sensitivity in or near welded areas to intergranular penetrations. In order to study more carefully the variables contributing to this attack, BMI prepared 12 experimental vacuum-melted nickel-base alloys having compositions not too dissimilar from that of Hastelloy F. These have now been delivered to Hanford, and preliminary testing has begun. Results indicate that the best of the 12 prepared alloys has the basic Hastelloy F composition but is stabilized with titanium rather than niobium.[18]

A second set of 12 experimental alloys will be prepared by Battelle to define more closely the limits of the constituent elements. All will be titanium stabilized.[19]

A second alloy considered for use at Hanford is Nionel. Experimental results on this material indicated that control of the impurity levels in this alloy might substantially improve its corrosion characteristics. Nionel prepared by vacuum-melting techniques was subsequently obtained, and corrosion tests were made.[50] Rates of attack in boiling Niflex dissolver solutions ($1M$ nitric acid—$2M$ hydrofluoric acid) were 75 mils/month for the vacuum-melted material as compared to 230 mils/month for conventional air-melted alloy.

The importance of the control of the environmental variables in corrosion testing again became very evident in a series of tests Hanford made with the experimental Battelle alloys and boiling Sulfex environments. The variable which in this case produced a wide range of experimental results was the condensing system used which in turn affected the amount of dissolved

air present. Corrosion rates obtained when using cold-finger type condensers were about 10 times higher than those obtained when Friedrichs condensers were used.[17]

In the pursuit of a single construction material for a dissolver for both stainless steel and zirconium dissolutions, corrosion tests have been made in Zirflex process solutions with titanium. The objective is to combine the Darex-Thorex process (for which titanium appears to be satisfactory) and the Zirflex process for zirconium fuels in a single titanium vessel. The corrosion of titanium in Zirflex dissolver solutions is about 500 mils/month. ORNL has learned that additions of $0.4M$ to $0.6M$ hexavalent chromium reduces this rate to 40 to 60 mils/month, whereas Hanford's experiences indicate that additions of $0.1M$ hexavalent chromium or $0.1M$ citrate has an inhibiting effect.[50]

The Perflex process is the most recent one to receive consideration for zirconium-base fuels. The dissolvent is $34.4M$ hydrofluoric acid $-0.6M$ hydrogen peroxide. Aluminum nitrate and nitric acid are added following dissolution to yield a stable solvent-extraction feed. Scouting corrosion tests have been made in $1M$ hydrofluoric acid $-0.05M$ hydrogen peroxide. The concentration of peroxide decreases with time, and this has a marked effect on corrosion rates. Hastelloy C appears to be the most promising material at the present time with a rate of 4 mils/month for 24-hr exposures and 19 and 60 mils/month for 4- and 1-hr exposures, respectively.[51]

The Idaho Chemical Processing Plant (ICPP) has the responsibility for handling the fuel from the Heat Transfer Reactor Experiment (HTRE) of the General Electric Aircraft Nuclear Propulsion Dept. This fuel is clad with Nichrome-V: 80 per cent nickel, 20 per cent chromium, and 1 per cent niobium. It has been proposed to dissolve this fuel in an acid mixture of 40 volumes nitric acid, 60 volumes hydrochloric acid, and 90 volumes water. A topical report has been published on the corrosion of titanium in this acid system.[52] One of the concerns in the use of titanium is hydrogen embrittlement due to the cathodic corrosion reaction. To magnify the possible susceptibility of titanium to hydrogen embrittlement, a $1\frac{1}{2}$-volt negative potential was applied to the specimens. (It would appear that the application of this potential would also afford cathodic protection to the specimen as a whole, thus giving lower over-all corrosion rates.) In duplicate experiments where electrically coupled and dissolving Nichrome-V were included, protection of the titanium was demonstrated. In the range of solution compositions of interest for the processing of HTRE fuel, the corrosion of titanium is quite acceptable. Resistance was poor where the mole fraction of hydrochloric acid exceeded that of nitric acid. The presence of Nichrome-V decreased the corrosion rate by a factor of 5 to 100. No knifeline or other type of localized attack was observed.

The Savannah River Laboratory has investigated the possibility that the Purex equipment of the Savannah River Plant could be utilized for Thorex processing. Since the bulk of this equipment is constructed of stainless-steel types 309SCb and 304L, corrosion tests were made of these materials in various Thorex environments.[53] In the initial dissolvent ($10M$ nitric acid $-0.05M$ to $0.10M$ hydrofluoric acid), corrosion rates were 200 to 400 mils/year. In the presence of dissolving thorium and with thorium concentrations of up to $1M$, the corrosion rate is considerably less: 10 mils/year (25 mils/year is considered acceptable). The recommendation is made that a heel of thorium be maintained at all times during dissolution. Other alloys were also tested in the beginning dissolvent; tantalum and stainless-steel types 309 and 310 corroded at rates less than that of 309SCb. However, the corrosion margin was considered insufficient to warrant replacing existing equipment. Parameters tested in greater detail are the effect of concentration of hydrofluoric acid and thorium nitrate, and the effect of welding. Figures 7 and 8 show isocorrosion curves in this system for both stainless-steel types 304L and 309SCb.[53]

Fluoride Volatility Processes

A new chemical processing system containing nitrogen dioxide, bromine trifluoride, and hydrofluoric acid has been investigated in the search for a low-temperature dissolution mixture suitable for a general fluoride volatility process. The method is potentially suitable for aluminum, zirconium, and stainless-steel clad fuels. A corrosion program is under way to determine which construction materials are useful in the associated environments.[22,54-57] In general, it appears feasible to process zirconium in 10 mole % nitrogen dioxide -75 mole % hydrofluoric acid at $110°C$, 2S aluminum in 25 mole % nitrogen dioxide in hydrofluoric acid at $150°C$, and
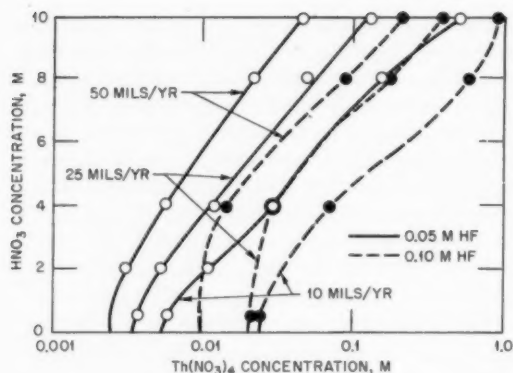
Figure 7 — Corrosion of 304L stainless steel in boiling hydrofluoric acid solutions containing nitric acid and thorium nitrate.[53]
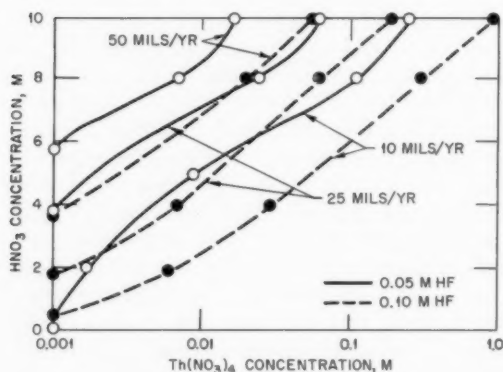

Figure 8 — Corrosion of 309SCb stainless steel in boiling hydrofluoric acid solutions containing nitric acid and thorium nitrate.[53]

stainless-steel type 304 in 55 mole % nitrogen dioxide in hydrofluoric acid at 150 to 200°C. Monel is the construction material under consideration. In a typical cycle involving Zircaloy-2 fuel, corrosion rates of Monel were on the order of 4 to 6 mils/month. For a comparable stainless-steel type 304 dissolution cycle, rates were 9 to 12 mils/month. The cycles include dissolution, evaporation of solvent, and the drying of salt. The rates in the stainless-steel test were approximately twice that obtained at a lower temperature of 115°C. Operating experience has shown that Monel systems closed to the atmosphere incur less corrosion than do systems opened periodically for removal of dis-

solver tubes, etc.[22] Tables IV-5 and IV-6 list some of the corrosion results obtained with nickel alloys tested. The contact of nickel and Monel specimens with dissolving zirconium has been found to be an important parameter in testing in the 25 to 75 mole % nitrogen dioxide – hydrofluoric acid mixture at 100 to 150°C. Simple contact did not affect the rates; however, moderate to very high corrosion rates over short periods were found when the Monel or

Table IV-5   CORROSION OF VARIOUS METALS IN 25 MOLE % NITROGEN DIOXIDE – 75 PER CENT HYDROFLUORIC ACID CONTAINING COMPLEX ZIRCONIUM SALT[55]

(Salt Content: 1.1 to 1.7 g per 20 ml; Time: 18 hr)

Material	Temp., °C	Corrosion rate, mils/month
Inconel	25	26
Inconel	50	47
Nickel	25	Gain
Nickel	50	0.8
Nickel	50	9.0
L Nickel	25	Gain
L Nickel	50	1.4

Table IV-6   CORROSION OF NICKEL AT 50°C IN NITROGEN DIOXIDE – HYDROFLUORIC ACID ENVIRONMENTS[55]

Solution composition, mole %			Corrosion rate, mils/month
NO$_2$	BrF$_3$	HF	
25		75	0.02
26	4	70	0.014
24	11	65	0.016

nickel specimens were wedged against dissolving zirconium: up to 190 mils/month.[56,57] Brief scouting tests were made on a variety of materials at 66°C. Nionel, gold, platinum, and Hastelloy N were found to be reasonably resistant, whereas tantalum, chromium, Haynes 25, Inconel X, and Illium G were attacked. At 150°C Nionel, 304 stainless steel, and Hastelloy B were unsatisfactory.[56]

At Argonne a rather basic program on the study of the reaction of fluorine with various metal surfaces is under way. Some of the first studies have been with nickel, and one of the primary objectives has been to determine the mechanism of attack.[24] It has been determined

by using radioactive Ni^{63} that the corrosion reaction proceeds by the migration of fluorine through the fluoride film to the nickel film interface. Ni^{63}, 2.5 μ thick, was plated on conventional nickel coupons which were then subjected to fluorine at 700°C. The position of the radionickel was then ascertained by autoradiographic techniques. Examination of the autoradiographs showed that the radionickel was concentrated at the surface of the film at the nickel fluoride–fluorine interface. Although the results indicate which species is doing the migrating, it has not been determined what state the fluorine is in during the migration, i.e., whether it is ionic, molecular, or atomic.

In several additional experiments, "A" nickel, which had been previously heat-treated under vacuum for $16\frac{1}{2}$ hr at 850°C, did not undergo intergranular attack when subsequently exposed to fluorine at 700°C for 64 hr. A-nickel coupons not so heat-treated were severely attacked.[24]

Pyrometallurgical Processing

The pyrometallurgical processing methods under study at Argonne involve molten-metal environments of magnesium-cadmium mixtures. Two medium carbon-steel thermal-convection loops were operated[24] for 144 and 1000 hr. The first of the loops circulated 30 wt.% magnesium in cadmium at 675°C with a temperature difference of 100°C. The hot leg was pitted and void of grain structure, indicating attack by solid solution of iron. The amount of metal transferred was estimated at 0.9 g. The second loop was operated with 15 wt.% magnesium in cadmium at 725°C and again with a temperature difference of 100°C. It was estimated that 6.4 g of iron was transferred. The efficiency of the mass transfer in this particular system appears sufficiently low to allow reasonable operating times without excessive corrosion in the equipment.

Waste Solutions

Corrosion programs for the various newly developed head-end processes usually include some studies directed to waste handling. In most of the environments the rates of attack are low enough to cause no concern with the alloys tested. The single exception is spent Sulfex decladding solution which, at 70°C and the boiling point, is sensitive to galvanic contact with mild steel.[50] This is unusual because the mild

steel of a steel–stainless steel couple more frequently becomes the anodic element of the couple and subsequently corrodes more rapidly while the stainless steel benefits from the resulting cathodic protection.

The Savannah River Laboratory studies of the corrosion of stainless steel in Thorex process solutions have also included experimental work on waste solutions.[53] The corrosion of stainless-steel types 304L and 309SCb was monitored in a series of nitric acid–hydrofluoric acid–sodium sulfate–sodium nitrate mixtures which simulate the changing concentrations of waste solutions during an evaporation step. The beginning solutions corroded these alloys at rates of less than 4 mils/year, but, where concentration factors of 4 to 6 were achieved, these rates increased to 60 and 110 mils/year for stainless-steel types 304SCb and 304L, respectively. The present waste evaporators at Savannah River are constructed of stainless-steel type 304L.

In other tests it was learned that additions of aluminum nitrate successfully complexed fluoride and reduced the corrosion during the evaporation step. The addition of hexavalent chromium to simulate the accumulation of dissolved stainless-steel corrosion products resulted in marked increases in corrosion. For types 304L and 309SCb stainless steel, the rate increased from less than 10 to about 600 mils/year by the addition of $0.10M$ CrO_3.

A topical report on the corrosion of carbon steel in waste solutions containing mercury has been published.[58] The waste solutions studied were from the Purex and "25" processes. Addition of either mercurous or mercuric nitrates did not increase the corrosion of these alloys in simulated waste-storage solutions. Rates of attack were generally below 4 mils/year. Vapor-phase attack was more severe than liquid-phase attack at boiling temperatures. Tests with the simulated 25-process waste solutions indicated that pits up to 8 mils deep are obtained in three months of exposure at 60°C. Solution composition does not appear to affect the vapor-phase results.

In a procedure developed at ANL, waste solutions are calcined by spraying into a fluid bed at high temperatures. In conjunction with further developments being done at Hanford, studies have been initiated on the corrosion of candidate construction materials for contact with calcined waste at high temperature.[18] Tests are conducted by exposing materials at 800°C to

acidic Purex wastes after (1) fluid-bed calcination and (2) batch calcination with sulfate additions. Materials tested to date include SAE 1020; stainless-steel types 304L, 309L, 316L, and 347; Hastelloy B and C; Nionel; and nickel. The fluid-bed calcined wastes were less corrosive by a factor of 2 than batch-calcined wastes, possibly due to the added sulfate in the latter. Only Nionel and stainless-steel type 304L corroded at a rate of less than 10 mils/month.

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Uranium Milling Wastes

A recent Winchester[1] report gives the current status of certain aspects of radioactive pollution problems associated with the uranium milling industry. The relative contributions of the isotopes of radium (Ra^{223}, Ra^{224}, and Ra^{226}) are shown to be dependent not only upon mill chemistry but upon the elapsed time between chemical treatment and the final radium analysis.

In clear, untreated liquid effluents from acid-leach systems, the concentration of Th^{230} will be quite significant and the concentration of its daughter Ra^{226} will be, in order of magnitude, a thousand times the permissible level as established by Part 20 of the Code of Federal Regulations. The procedure recommended as effective for reducing Ra^{226} to permissible concentrations is neutralization and barite treatment. For acid flow-sheet effluents, neutralization to a pH of 8 will effectively remove Th^{230} from solution and reduce Ra^{226} substantially. A subsequent multistage countercurrent treatment, deep-bed percolation, or column treatment of the neutralized solution employing approximately 0.3 g of barite per liter of effluent removes 98 per cent of the remaining Ra^{226}. The two steps will remove Th^{230} and Ra^{226} sufficiently from acid-leach plant liquid effluents to make them comply with the prevailing and proposed regulations for these isotopes. Essentially 100 per cent of the radium and thorium values would then be associated with the tailings solids.

In the case of alkaline flow sheets, the addition of copperas ($FeSO_4 \cdot 7H_2O$) has proved to be effective in removing approximately 89 per cent of the radium from unneutralized effluents. This was accomplished by a two-stage copperas treatment (each stage employing 0.1 g of copperas per liter) with adequate settling between stages. Further radium removal, if required, may be achieved by a barite-treatment step.

Employing a countercurrent percolation of neutralized effluents through a bed or column of barite, the requirements for +65 −100 mesh barite amount to 0.3 g per liter to achieve a 98.5 per cent average removal of radium. The estimated chemicals cost for this treatment would be roughly 5 to 10 cents per ton of clear tailings pond effluent for the neutralization and 1.5 cents per ton for barite treatment, giving a total of 6.5 to 11.5 cents per ton of the effluent.

For alkaline flow sheets a two-stage copperas treatment employing 0.1 g per liter per stage would remove 80 to 90 per cent of the radium and would be expected to cost about 1 cent per ton of solution. Since this will probably not prove to be adequate for radium removal, this treatment could logically be followed by a barite-bed percolation stage which should cost approximately 1 cent per ton of solution for barite consumption, giving a total reagent cost of 2 cents per ton of alkaline effluent.

Reduction to Solids

Adsorption of activity on clinoptilolite (special adsorption clay), more work on various calcination schemes, and yet another report on temperature use in stored waste solids are reviewed here.

Adsorption on Natural Materials

The use of beds of clinoptilolite at Hanford for the decontamination of wastes contaminated with low concentrations of cesium has been mentioned in the last two Reviews.[2,3]

The effect of the accompanying ion on the adsorption of cesium by clinoptilolite was studied within the cesium concentration range[4] of 10^{-6} to $0.1M$. Cesium concentrations in most wastes will be less than $10^{-2}M$ and in low-level wastes will usually be present as a "trace" such as in Columbia River water (concentration about $4 \times 10^{-9}M$ cesium). Experiments were conducted with clinoptilolite columns receiving solutions containing $1.0M$ Na^+ and various cesium concentrations. The number of column volumes

of effluent required to achieve a 50 per cent breakthrough was used as a measure of mineral capacity in each case. The number of column volumes required increased with decreasing concentration down to $10^{-3} M$ cesium. Below this, the number of column volumes required to reach 50 per cent breakthrough remained constant, implying a constant distribution coefficient in that concentration range. A pilot plant to test this process has been completed, and a cold shakedown run has been finished.

Calcination

The Hanford program of studies in the 8-in. by 10-ft radiant-heat spray calciner continued (references 2, 3, and 5 to 7). Significant additional results[8] were as follows:

1. Feed rates were increased to 6.3 gal/(hr) (sq ft) with simulated formaldehyde-killed Purex waste and to 11.4 gal/(hr)(sq ft) with neutralized waste. Residual nitrate increased from a value of <0.004 per cent at 4 gal/(hr)(sq ft) to 0.04 per cent at the highest rate, and weight loss on subsequent heating (for one-half hour at 900°C) increased from a value of 31.5 per cent to 35.1 per cent.

2. Ammonia neutralization (rather than NaOH) was tried successfully in one run. This substitution has the important advantage of eliminating sodium ion (which increases solubility and leachability of the calcined residue) and sodium nitrate (whose wide liquid range complicates calciner operation). Formaldehyde-treated waste was neutralized with aqueous ammonia, and the slurry was calcined without sugar or other additives. Operation was uneventful, and the product was more compact than that obtained either with acidic waste or caustic-neutralized waste. The total weight of residue was also decreased (from 200 g per liter of acidic waste to 150 g per liter of ammonia-neutralized waste), apparently owing to greater destruction of sulfate.

3. The ceramic filters have continued to give trouble, due to leaks around the gaskets or to cracking caused by differential thermal expansion. A cyclone was tried but failed to work well. A different approach consists of eliminating the filters and condensing the condensable material with the powder product, followed by evaporation to dryness in the final storage container. This treatment has the added advantages of a two- to threefold increase in product density (as compared to as-produced powder) plus an increase in thermal conductivity. Advantages over pot type calcination include elimination of foaming and of danger of off-gas line plugging.

The Hanford fluid-bed waste calciner[3] is designed to process simulated Purex first-cycle waste at temperatures of 350 to 600°C at maximum feed rates of 25 to 40 liters/hr. Figure 9 is a process flow diagram of the facility.

The calciner heating section is 8 in. square and 36 in. high and is heated by 54 horizontally mounted Inconel-sheathed internal electrical resistance heaters, each rated at 1100 watts.

The feed is introduced through one or more of several nozzles (standard commercial siphon type with pneumatic atomization) which are mounted on the sides of the calciner immediately above the heaters. Air and steam are to be used for atomization of the feed. The calcined granules may be removed via two adjustable-height side overflow lines or by a bottom take-off line.

The calciner bed is fluidized by air or steam preheated in a 4500-watt electrical resistance heater and distributed through a bubble-cap distributor plate.

The off-gas equipment initially installed is quite conventional and is designed to provide satisfactory gas cleanup in the existing radioactivity-free system but would not be adequate in a system containing radioactive materials. Space, piping provisions, and plans have been made for later testing of various types of efficient particulate cleanup devices.

More than a dozen runs, using simulated formaldehyde-killed threefold concentrated Purex waste as feed, have been completed.[4,8] The primary problem continues to be the buildup of lumps on the feed nozzle.

Variations in operating temperature from 400 to 600°C showed no significant effect on nozzle buildup. Atomizing air-to-feed flow ratios of about 600 are sufficient to keep nozzle buildup and lump formation to near the acceptable level but result in an undesirably small average product particle size. Lower atomizing air-to-feed flow ratios give a more desirable average product particle size but also result in excessive nozzle lump formation. One run using aged feed solution which had precipitated was performed without difficulties due to the slurry.
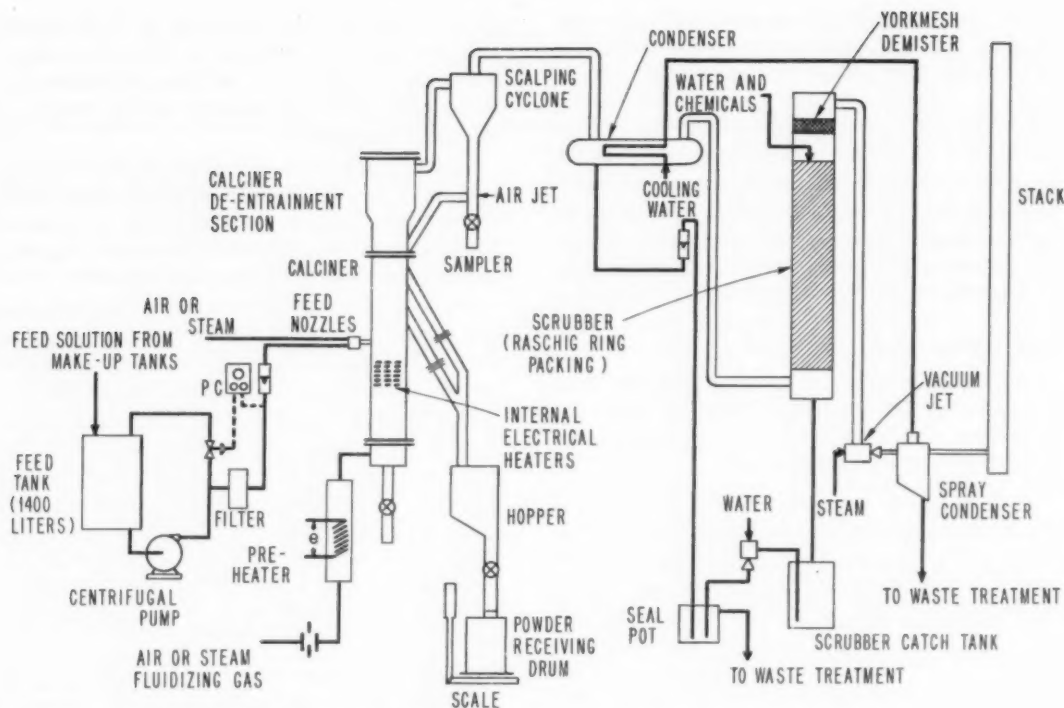
Figure 9—Hanford fluid-bed-calciner simplified process flow diagram.[9]

Final Disposal Method

Sea Disposal

The British are making by far the most extensive use of sea disposal, and they are at the same time providing the best environmental survey information available on the effects of such disposal.[5,10] They are now building a third pipeline at Winfrith on the south coast of England.[11] The other two are at Windscale (on the Irish Sea) and at Dounreay (on the north coast of Scotland).

Technical information on the Winfrith pipeline can be summarized as follows:

1. Over-all length, 7 miles.
   a. 5 miles overland, pipeline buried 3 to 8 ft below the surface.
   b. 2 nautical miles on the sea bed.
   c. Twin pipeline, each line consisting of 7-mile-long inner pipe (6 in. in diameter) and an outer pipe (12 in. in diameter). The 5-mile-long outer pipe ends 50 ft below Low Water Springs (near the point of entry to the sea).

2. Point of entry to the sea, Arish Mell.
3. Authorized discharge rate, 2500 curies a calendar month with a maximum of:
   a. 750 curies of Ru^{106}.
   b. 100 curies of Sr^{90}.
   c. 100 curies of total alpha activity.
4. Total volume of effluent:
   a. 400,000 gallons of active effluent a day.
   b. A maximum capacity of 1.1 million gallons of nonactive effluent a day.
5. Specific activity of the radioactive effluent, assuming uniform release rates as shown in 3 and 4a, is 0.05 μc/ml.
6. Estimated radiation dose rate above a section of pipe carrying effluent, buried 3 ft below the surface, is 0.05 μr/hr. This can be compared with the radiation arising from natural earth which is of the order of 5 μr/hr measured at a height of 1 meter.
7. The total estimated cost of the pipeline installation comprising the sea disposal tanks on site, pumphouse No. 1 on site, and the pipeline with a valve house on the coast is approximately one million pounds ($2.8 million).
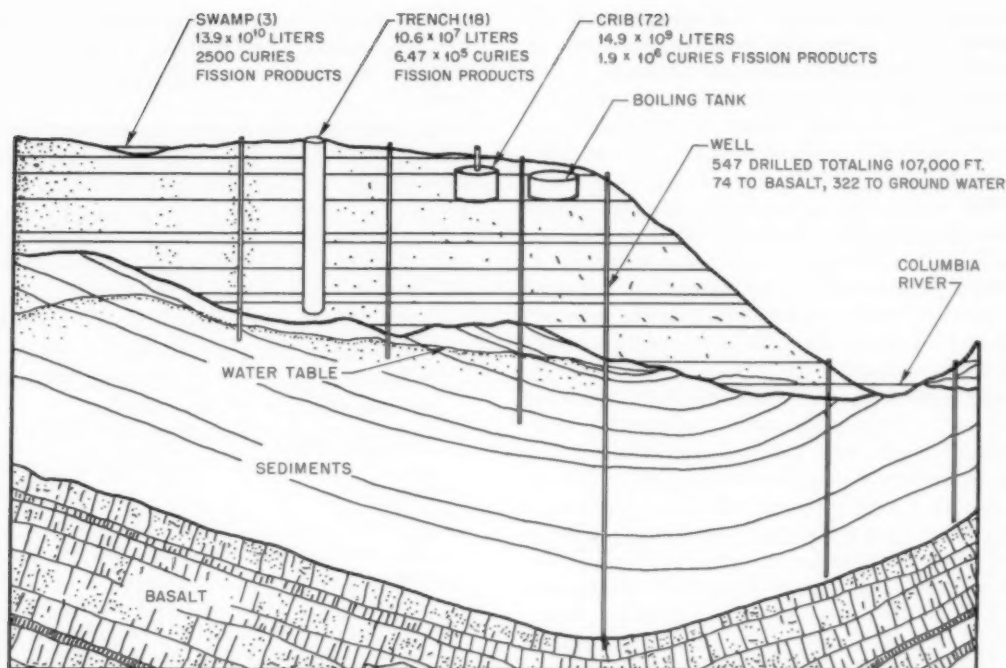
Figure 10 — Hanford site cross-section schematic showing waste-disposal facilities.[12]

Ground Disposal Experience

The separations plants at Hanford discharge large volumes of solutions containing radioactive materials to various ground disposal facilities.[12] The largest contribution to the waste volume is made by the process cooling-water streams. These discharge to naturally occurring depressions in the ground surface which are locally called "swamps." This waste is normally uncontaminated but infrequently contains low-level contamination due to corrosion failure of process equipment. The present recommended maximum limit for radioisotopes in wastes sent to swamps is 5×10^{-5} μc beta emitters/ml. To date a total of 139 billion liters (36.7 billion gallons) and about 2500 fission-product curies have been discharged to three swamp sites.

Trenches are once-used facilities into which high salt wastes or wastes containing complexed radioisotopes are discharged. The effectiveness of the disposal depends upon the "blotter effect" or the "specific retention" properties of the dry Hanford soils. To date 18 trench sites have received 106 million liters (28 million gallons) of waste containing 647,000 curies of fission products.

Process condensate wastes which generally contain radioisotopes in concentrations of 1×10^{-1} to 1×10^{-3} μc beta emitters/ml and those wastes which have the potential of being highly contaminated are discharged to subsurface cribs. The classical crib design was a boxlike timbered structure, whereas more recent types have trapezoidal cross sections and may vary in length from 20 to 1600 ft. They are filled with washed and sized gravel to promote even distribution of the waste solution. The wastes are piped into them underground, and from them the wastes percolate through the soils toward the water table. The effectiveness of this disposal method depends upon the ion exchange of the radioisotopes with the soil. A total of 72 crib structures has received 14.9 billion liters (3.95 billion gallons) containing 1.9 million curies of fission products. The various ground disposal facilities, including sampling wells, in use at Hanford are shown schematically in Fig. 10. These large volumes of wastes dis-

charged to ground have resulted in a certain degree of ground-water contamination and in the formation of "ground-water mounds."

Ground-water contamination concentrations range from as low as 1.5×10^{-7} μc beta emitters/ml alongside the cribs. The maximum observed was 6.0×10^{-2} μc beta emitters/ml.

Most of the radioactive material in the ground water is ruthenium. However, small amounts of Cs^{137}, Co^{60}, and Sr^{90} have also been detected. In 1956, Co^{60} and Cs^{137} were detected in the ground water at distances up to 1000 ft from the disposal point. At that distance the concentrations were 1×10^{-5} and 1×10^{-6} $\mu c/ml$, respectively. At the present time, Cs^{137} is no longer detected and Co^{60} is found in seven wells immediately adjacent to the crib site; the maximum detected concentration of Co^{60} is 2.1×10^{-4} $\mu c/ml$.

At Oak Ridge, intermediate-level wastes are disposed to pits from which the liquids percolate into the Clinch River via White Oak Creek.[13,14] From June 1952 through December 1958, a total of 1.17×10^7 gallons of waste, containing about 158,000 curies of beta radioactivity, was pumped to the pits. Although Cs^{137} and Ru^{106} continued to be the principal contributors to radioactivity in the waste, in 1958 there was a significant increase in the amounts of Sr^{90} and total rare earths. Totals of approximately 10,000 curies of Sr^{90} and 90,000 curies of rare earths have been released to the pits.

The importance of the increased amount of Sr^{90} in the wastes lies in the potentially hazardous contamination of the Clinch River. If all the waste released to the pits in 1958 had been released to the river, and if complete mixing had occurred, the maximum permissible concentration for drinking water for continuous occupational use would have been exceeded by a factor of 2. However, the pits have reduced significantly the potential hazard to the Clinch River since the soil around the pits continues to retain the strontium and cesium.

It is estimated that 160 curies of Ru^{106} escaped from the pits into the bed of White Oak Lake in 1958, compared to 200 curies released during 1957. An inventory of the nonradioactive chemicals revealed that about 200 tons of nitrates escaped from the pits in 1958. It is further estimated that the average concentration of ruthenium in the Clinch River with complete mixing would be about 1.5×10^{-8} $\mu c/ml$, 3.5 per cent of the maximum permissible concentration for drinking water for continuous nonoccu-

pational use. Similarly, the amount of nitrates escaping from the pits would result in concentrations in the river of the order of 0.04 mg/liter.

In order to estimate the land-usage requirements for low-level solid waste, records of solid-waste burial dating back to 1957 had been analyzed.[14] These data were extrapolated, and estimates of the volume of waste expected in the next five years were made. These are summarized in Table V-1.

Table V-1   ESTIMATED VOLUMES OF SOLID
RADIOACTIVE WASTE[14] FOR 1959 THROUGH 1964
(In Thousands of Cubic Feet)

Year	Alpha waste	Beta-gamma waste	Total
1959 (last half)	63	77	140
1960	197	163	360
1961	194	173	367
1962	237	186	423
1963	224	193	417
1964	262	201	463
Total	1177	993	2170

To simplify and improve monitoring, a new waste-disposal trench design has been adopted for disposal of solid waste. The bottom of the trench is covered with 6 in. of gravel and sloped to an asphalt-lined sump at one end in which a 6-in. perforated casing is installed. Any liquid entering the trench will flow through the gravel underdrain to the collecting sump, from which samples can be withdrawn and analyzed. After the trench is filled with waste, the void space around the contaminated material is backfilled with shale. A layer of shale near the top of the trench is compacted by tamping, providing a base for an asphalt cap. About 1 in. of asphalt is sprayed on the tamped shale, and, after the asphalt hardens, the remainder of the opening is backfilled with shale. After filling of the trench, the composition and amount of the liquid collected in the sump will be used to evaluate the extent of leaching of radioactive materials from the waste and will serve as an indicator of the effectiveness of the asphalt cap in diverting rainfall.

Disposal into Salt Formations

The experimental program of field study of disposal into salt formations, coordinated by

ORNL, has been described in previous Reviews.[5,6] Oak Ridge National Laboratory has entered into contractual arrangements with the Carey Salt Co., Hutchinson, Kansas, for use of an unoccupied section of their mine to carry out these field experiments. The test facility for the first experiment consists of two 7.5-ft-square by 10-ft-deep cavities in the floor of the mine, off-gas covers, off-gas collection equipment, heaters, power recorders, controls, and instrumentation. The size of the cavities was selected so that the surface area when the cavity is filled to a 7.5-ft depth will be equal to that of a 10-ft-diameter sphere. Thus thermal data from the theoretical heat calculations already made can be correlated with thermal data from the experiments.

The operating level of the Carey mine is about 640 ft below the earth's surface, and all equipment must be fabricated to sizes that can be brought down the mine shaft. This restriction limits the dimensions of any equipment to about 5 by 6 ft. Equipment will be reassembled and installed in the experimental area of the mine.

In March 1959 field work was initiated in the Carey mine to prepare the site for these first field experiments. The first pit has been excavated, and equipment is being installed, but because core drillings indicate that the subfloor in this location is not pure salt (therefore the pattern of heat dissipation will be different from that predicted from theoretical calculations), two 1:50-scale models of the field experiment will be run in the 6-ft layer of pure salt in addition to those planned for the larger installations.

Hazards Evaluation
of Tank Storage

In its annual report[14] for fiscal year 1959, the Health Physics Division of ORNL has made an attempt to analyze the hazard of storing wastes. In view of the fact that tanks are being used to store present-day waste and will probably continue to be used for some years, it was decided to initiate a series of waste-disposal hazard studies, beginning with the hazards of tank storage. It was decided that the study should be limited to an investigation of possible consequences of a tank failure and not to the probability or mechanism of the failure itself.

For this study a site was chosen which lies on a broad plateau of low relief. The general elevation of the Ohio River which flows nearby is 420 ft. The valley wall of the Ohio River is quite steep and is highly dissected by tributary streams which have cut deep, narrow valleys into the upland surface. The site, about 7 square miles in area, is bounded on the east by the river.

A tank size of 4×10^5 gallons was chosen. However, later studies pointed out the difficulty of cooling a tank of this size with wastes of the concentrations specified. By standard methods the activity in curies at any storage tank following the filling period was computed. These calculations were carried out for each of the important fission products and for the heavy elements, and the results are shown in Fig. 11.
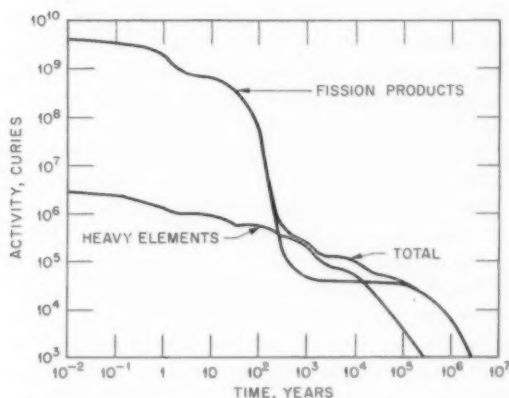

Figure 11 — Fission-product and transuranic activity.[14]

It is interesting to note from Fig. 11 that the transuranic elements contribute the majority of the activity for all times greater than 400 years and the majority of the activity starting at about 400 years and lasting for a period of approximately 20,000 years. Likewise, from the standpoint of maximum permissible concentration (MPC) in drinking water, the transuranic elements are the major contributors between 400 and 100,000 years.

The only type of accident so far considered has been the sudden release of the entire contents of the tank at a point below the surface of the ground. A release of this magnitude could result from such causes as earthquakes or sabotage, as well as from explosions resulting

from chemical reactions or internal pressure buildup.

It seems evident that the wastes would not get into the Ohio River as a single dose but undoubtedly as a more continuous flow. The ground-water system will act as an averaging reservoir so that the large quantities of fission products will be passed out of the reservoir at a relatively constant rate over a substantial period of time.

A detailed analysis of the fate of contaminants released to the river would require a knowledge of the hydraulics, temperature, velocity, and pollution distribution in the river. This information is unfortunately not all available. In fact, the data are so nebulous that a sophisticated analysis is unwarranted, and simple dilution factors were used to calculate the concentrations downstream from the point of entry. Assuming complete dilution in the river, the concentration at any point and at any time may then be determined only if the rate at which the material is introduced into the river is known. This in turn depends upon the rate and direction of ground-water movement, as well as upon the interactions between the waste and the soil. An upper limit to the concentration may be obtained by assuming that the tank contents are introduced directly into the river in a short period. If the tank rupture were to occur under conditions that permitted channeling in the till, then it would be possible for the waste solution to come in intimate contact with the underlying bedrock which is already known to contain relatively large openings. Such an accident would afford minimum contact between the waste and the unconsolidated till while possibly introducing the waste directly into the openings in the limestone. A less severe accident can be postulated by assuming that the contents of the tank are emptied into a ground-water reservoir of the tank which feeds either directly into the river or into a surface stream which empties into the river.

Therefore the concentrations at the first city downriver have been calculated for various fractional leakage rates from the reservoir to the river. These values are shown in Fig. 12, wherein the parameter f is the fractional leakage rate from the reservoir. The MPC of the radiocontaminants of drinking water is also strongly time-dependent since the composition of the mixture continues to change with time. This time-dependence of MPC is also shown in
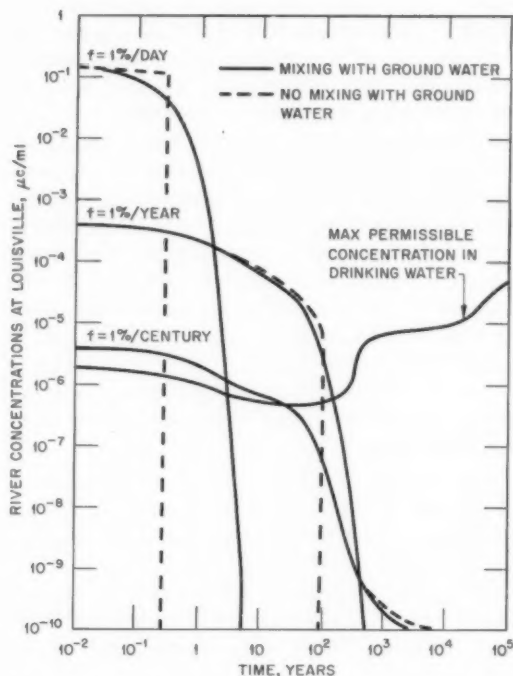

Figure 12—Calculated river contamination at the first city downstream.[14]

Fig. 12. There are several factors of safety which were not taken into account in the analysis. The most important of these is the neglect of the removal of radiocontaminants by ion exchange within the till and the mechanical filtering action of the sod.

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PRODUCTION OF URANIUM, THORIUM, PLUTONIUM,
AND THEIR COMPOUNDS

Uranium

Green-Salt Production

The conventional process for the production of uranium tetrafluoride, or green salt, involves the preparation of the compounds uranium trioxide, uranium dioxide, and uranium tetrafluoride in series. Development work continued at Mallinckrodt Uranium Division (Weldon Spring, Missouri) on fluidized-bed processes for uranium trioxide and uranium dioxide.[1] In operations of the experimental fluid-bed denitrator with highly concentrated uranyl nitrate feed liquor, 25 tons of trioxide was produced during a four-week period. Results showed that the denitrator is capable of consistent and reproducible operation. The fluidizing gas flow has a marked effect on the particle-size distribution of the product, and there is apparently an optimum velocity for the production of uranium trioxide with a narrow particle-size distribution. An increase in the amount of sulfate in the feed liquor increased the average particle size of the product.

The fluid-bed reduction reactor containing an internal tapered mandrel[2] has been run at rates up to 120 lb of uranium dioxide per hour per cubic foot of bed using fluid-bed denitrated uranium trioxide as feed. High assay uranium dioxide was produced, and the results indicate a higher productivity may be possible.[1]

This work and other development work in the United States is aimed toward highly improved processes for eventual replacement or expansion of existing equipment.

At the Fernald (Ohio) Feed Materials Production Center, plant-scale tests were performed on continuous pot denitration of uranyl nitrate.[3] A conventional batch denitration pot ($5\frac{1}{2}$ ft in diameter) was modified by the addition of two steam-cooled uranyl nitrate feed tubes and a central vacuum-transport tube for product removal. Production rates equal to those obtained by batchwise operation were attained without

difficulty, at reactor temperatures much lower than those required in the batch process. There were no indications at any time during the runs that scale was forming on the inside surface of the pot or that the maximum throughput with respect to heat transfer had been approached. The reactor shell was subjected to much less severe thermal treatment than in the batch process; therefore pot life should be greatly prolonged. Difficulties with the vacuum-transfer system pointed to the desirability of incorporating overflow product discharge facilities in this process. The oxide produced was dense, spherical, and low in chemical reactivity, but it is believed that product quality can be increased by improved operating techniques.

Drying of Uranium Tetrafluoride

A program pointed toward lowering the hydrogen content of uranium metal by removing water from the uranium tetrafluoride in a fluid-bed dryer has been inaugurated at Mallinckrodt's Weldon Spring Plant.[1] The average hydrogen content of as-reduced uranium metal has been correlated with the hydrogen content of uranium tetrafluoride in the bomb charge. The water content of green salt varies with the atmospheric dew point and normally runs 20 to 30 ppm in winter months and 50 to 200 ppm in the summer. Experiments were performed to control the hydrogen content of the uranium tetrafluoride by thermal degassing in a fluid bed using dry air as the fluidizing medium. Batch runs were made in a 6-in.-diameter bed charged with 20 lb of tetrafluoride to investigate the effects of temperature, time, and dew point of the fluidizing air. The superficial air velocity in each run was approximately 0.3 ft/sec at standard conditions.

It was concluded that the hydrogen content of uranium tetrafluoride received from the production plant can be controlled below 15 ppm in a fluid-bed dryer operated within the temperature range 120 to 260°C using dry air at an

initial dew point of $-50°C$. The results suggested that the drying rate was not greatly affected by temperature and that an elapsed time of approximately 18 min is sufficient to reduce uranium tetrafluoride from 130 to 15 ppm hydrogen as water. An empirical relation between the relative humidity of the air and the residual hydrogen content of the fluidized uranium tetrafluoride is also presented by the authors.

The primary variables of air, velocity, bed temperature, and dew point of the entering air were not optimized in these experiments. The intent was to explore an operating range for uranium tetrafluoride drying as a basis for expansion of the program to full-scale production. As a second step, a program has been initiated in which uranium metal is being produced experimentally from fluid-bed-dried uranium tetrafluoride.

Recovery of Magnesium and Anhydrous Hydrogen Fluoride from Magnesium Fluoride Slag

Anhydrous hydrogen fluoride and magnesium metal are raw materials which contribute substantial costs to the uranium-metal production operation. The recovery of these materials from magnesium fluoride slag from the uranium-reduction operation represents a potential means of reducing costs. Experiments are being conducted by the National Lead Company of Ohio on the reduction of slag by calcium carbide to produce magnesium metal and on the reaction of slag with sulfuric acid to generate hydrogen fluoride.

Laboratory experiments on a 100-g scale demonstrated essentially complete reduction of magnesium fluoride with calcium carbide at $1000°C$ and $350\ \mu$ absolute pressure. The raw magnesium after melting and fluxing appears to be satisfactory for use in reduction of uranium tetrafluoride to metal. The experiments were performed in a stainless-steel retort containing a boat with the reactant mixture. The magnesium vapors produced by the reaction were condensed on carbon-steel sleeves at either end of the reaction tube.

Later experiments were run in a plant-scale retort of the type currently used in magnesium production by the Pidgeon process. These tests confirmed the technical feasibility of the process for preparation of magnesium metal. However, the results indicated no apparent improvement over the conventional dolomite-ferrosilicon process with respect to operating temperature, pressure, cycle-time, and materials-handling considerations. Therefore the calcium carbide–magnesium fluoride process does not appear to be competitive with current practice.

Experiments on the reaction of sulfuric acid with slag were conducted on a 400-g scale. The preferred method involves the use of a stoichiometric quantity of acid. Reaction for 30 min at $200°C$ produced hydrogen fluoride in 40 per cent yield. The reaction residue, probably consisting of the acid fluoride of magnesium, was then thermally decomposed by calcination at $370°C$ to yield additional hydrogen fluoride. The over-all yield for both steps was about 80 per cent.[4]

Uses for Depleted Uranium

The amount of uranium that is discharged as gaseous-diffusion-plant bottoms depleted in U^{235} greatly exceeds any anticipated nuclear uses as a source material for at least 40 years. Some of the potential nonnuclear uses for depleted uranium were reviewed previously.[5] Factors controlling the present and future nonnuclear uses of uranium are discussed in a more recent report.[6]

Radiation and chemical toxicity of depleted uranium appear to be hazards which can be satisfactorily reduced through similar safeguards. The hazards are similar to those encountered in many heavy-metal industries and do not make remote handling of uranium necessary. The high atomic weight and density of uranium metal suggest uses for radiation shields, X-ray tube targets, and counterweights. The use of depleted uranium metal as an alloying metal and as a strong reducing agent appears promising but is not yet of commercial importance. Possible uses of uranium metal for cathodic protection or as a constituent of steels is now under investigation by the U. S. Bureau of Mines.

The most important potential use for depleted uranium hexafluoride is as a source of fluorine. Several processes under development recover fluorine in a hydrogen fluoride product with 100 per cent yields of hydrogen fluoride containing a variable amount of water, and process improvements can be expected to minimize the dilution.[5] The other product, uranium oxide, has two important commercial uses, as a ceramic pigment and as a refractory. The present

use for uranium oxide as a pigment should continue or expand slightly, and the present extensive research on the ceramic properties of uranium dioxide (carried on to develop improved reactor fuels) should provide valuable data for a greatly increased use of uranium dioxide as a refractory.

Thorium

Thorium Oxide

The preparation of dense, spherically shaped thorium oxide particles in the size range of 100 to 500 μ has been attempted at Oak Ridge.[7] The primary interest in this size of oxide is for studies of a heavy- or light-water fluidized-bed nuclear reactor blanket. Results reported for denitration of uranyl or aluminum nitrate in gas-fluidized and mechanically agitated beds[8] indicated the possibility of obtaining an oxide product with the desired properties by feeding thorium nitrate solution into a high-temperature bed of thorium oxide particles.

In a series of runs in fluidized-bed denitration equipment, aqueous and methanol solutions of thorium nitrate were sprayed into a fluidized bed containing either sintered thorium oxide agglomerates or classified sea sand. The variables studied were feed concentration (1.5M to 2.5M), fluidizing air velocity (0.6 to 1.3 ft/sec), and bed temperature (400 to 700°C). The yield of fines was high in all runs, and bed caking was a problem in all runs except that with a bed temperature of 700°C.

An agitated-trough denitrator was operated over a temperature range of 150 to 300°C with similar results. The trough agitator blades moving at a maximum velocity of 1.85 ft/sec prevented caking in this calciner, but the yield of oxide fines was not reduced in the trough compared to the fluidized bed.

The results of the studies did not indicate that either the fluidized bed or the agitated trough is feasible for producing dense high-strength thorium oxide spheres in the desired size range. Operating conditions for spray-calcining thorium nitrate in an agitated bed of solids and obtaining oxide particle growth are evidently more critical and difficult to attain than the conditions for similarly calcining uranium nitrate. The thorium denitration reaction appears to deposit oxide agglomerates (size range 20 to 30 μ) on the existing bed particles

which can be removed by attrition within the bed. The process may be feasible for the production of finer thorium oxide of less exacting physical specifications.

Plutonium

Plutonium Trichloride Process

Plutonium metal is currently produced by calcium reduction of plutonium tetrafluoride.[8] The development of a reduction step using plutonium trichloride instead of plutonium tetrafluoride was proposed to reduce the neutron radiation associated with plutonium fluoride [neutrons are produced by (α,n) reaction on fluorine]. Measurements showed that a sixty-fold reduction in neutron flux could be realized by converting to a chloride process. Chloride processes are now common in the metal preparation industry, and development work at Hanford has shown that plutonium trichloride can be satisfactorily prepared and reduced to the metal.

To complete this work, a process for recovering plutonium from the chloride slag and crucible material obtained from metal-reduction wastes was needed. This method would be adaptable to the recovery of other plutonium-bearing chloride waste salts, such as might be obtained in the electrolytic reduction of plutonium in fused-salt baths. The plutonium recovered must be suitable as feed for solvent extraction or ion-exchange purification in a nitrate system.

The process starts with a nitric acid dissolution of plutonium and other solids containing halogens. The corrosive halogens are simultaneously boiled off to produce a solution suitable as feed for solvent extraction or ion-exchange processing. This step does not result in complete dissolution of the plutonium. Filtration of the solution is necessary, and the insoluble solid (containing up to 30 per cent plutonium but only about 3 per cent of the initial solids) is dissolved in nitric-hydrofluoric acid. Aluminum nitrate is added to complex the fluoride before the solution is fed to the extraction process. Total waste losses average 0.7 per cent, but this can be reduced further to 0.01 per cent by a second treatment of the residues with nitric-hydrofluoric acid. Chloride is reduced to 35 ppm, or well below the limit for chloride in the solvent-extraction feeds. An

alternative process involving some modifications of the above procedure is also described by the authors.[9]

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